

# Electroluminescence from polyvinylcarbazole films: 4. Electroluminescence using higher work function cathodes

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Following the previous demonstration of electroluminescence emission from polyvinylcarbazole (PVCz) films having caesium cathodes, the possibility of using less chemically reactive higher work function cathodes was studied. It is shown that this can in principle be accomplished by the use of suitable electron-accepting additives in the PVCz films and a range of cyanobenzene molecules was used for this purpose. The fluorescent properties of the exciplexes and exterplexes inevitably formed between the cyanobenzene acceptors and the carbazole donor groups of the PVCz were investigated in order to determine the most suitable additives. Acceptor anions and carbazole cations in PVCz films were observed spectroscopically at low temperatures as was their recombination luminescence on subsequent warming. Finally, electroluminescence was observed from PVCz films containing cyanobenzene additives and using cathodes of barium or calcium.

**Keywords** Electroluminescence; polyvinylcarbazole; cyanobenzene electron acceptors; exciplexes; fluorescence; thermoluminescence

## INTRODUCTION

The development of an electroluminescent device based on the use of a double-layer polyvinylcarbazole (PVCz) film was described in paper 3 of this series. In this device electrons and positive charges were injected into opposite sides of a PVCz layer and their mutual recombination formed excited molecular states which then reverted to the ground state with luminescence emission. However, in order to inject electrons into the PVCz film (in which the electrically and chemically active components are the carbazole groups, which themselves have virtually zero electron affinity in the gas phase) it was necessary to use a very low work function cathode made of caesium. The high chemical reactivity of caesium and the other alkali metals make this a very inconvenient arrangement in practice. However, use of a higher work function more stable cathode material would require a corresponding increase in the electron affinity of the polymer film if injection is still to occur. As there are few, if any, polymers of appreciable electron affinity and electrical conductivity together with the necessary luminescence properties, it was decided instead to concentrate upon organic molecules of appreciable electron affinity which could be used as additives in a PVCz film.

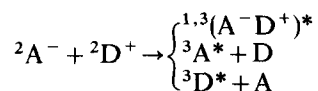
## DESIGN

The addition of molecules of considerable electron affinity ('acceptors') to a polymer like PVCz containing molecular groups of comparatively low ionization potential ('donors') is known to give rise to the formation of a

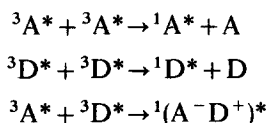
charge-transfer complex<sup>1</sup> in which there is a partial donation of an electron from each donor to its paired acceptor molecule. If the degree of donation is sufficient to bind the donor and acceptor into a stable pair, then a new absorption band will appear to the red of the lowest absorption band of either separate molecule. This is due to an electronic transition from the stable ground state of the complex to its excited state. Emission is in general possible by the reverse transition process and this will likewise be to the red of any (fluorescence) emission from either molecule separately. If the charge-transfer interaction is very weak then a stable ground state of the complex may not be formed at all yet complex formation may still be possible in the excited state. In a species of this type, known as an excimer if both molecules are identical or an exciplex if different, there is no charge-transfer absorption band, since no stable ground state exists, yet there can be emission from the excited state to a transient ground state and again this is red-shifted relative to the fluorescence of either component. It is found in practice that the fluorescence efficiency of exciplexes is highest for emission at the blue/green end of the visible spectrum and that it falls off rapidly for emissions towards the red region due to a sharply increasing probability of radiationless transitions as the energy separation between ground and excited states narrows.

For electroluminescence production it is necessary that recombinations between acceptor anions and donor (carbazole) cations shall produce luminescence and recombination energy criteria will thus have to be met, just as for the case of carbazole anions and cations discussed in paper 3. Chemiluminescence<sup>2</sup> and electro-

chemiluminescence<sup>3</sup> studies have shown that the recombination of acceptor anions with donor cations may produce several different products:



where  $(A^-D^+)^*$  is the exciplex (or excited charge-transfer complex if it has a stable ground state) while  ${}^3A^*$  and  ${}^3D^*$  are the triplet states of the isolated acceptor and donor molecules respectively. Singlet excited states of donor and acceptor molecules are not included here as their direct formation is normally blocked because their energies are higher than the energy available from ion recombination. However, such states, together with additional exciplex states, can often be produced by triplet-triplet annihilation:



The ion recombination energy  $R$  is given by the energy required to produce a separate anion and cation which (from paper 3) is in solid phase:

$$R = (I_G - \chi_G) - P^+ - P^- \quad (1)$$

where  $I_G$  and  $\chi_G$  are the gas-phase ionization potential and electron affinity of the donor and acceptor molecule respectively while  $P^\pm$  is the stabilization energy of a unit charge on a particular molecule caused by its polarization of the surrounding medium (since different molecules are used for the anions and cations somewhat different polarization energies are likely). As  $\chi_G$  will have a substantial value for any electron acceptor molecule as compared to the virtually zero value for carbazole, there will be less recombination energy available than in the previous case of recombination by carbazole anions and cations and direct formation of singlet carbazole excited states thus cannot be expected. It is also unlikely that carbazole triplets will be formed since taking  $I_G$  as 7.4 eV for carbazole and  $P^\pm$  as 2.1 eV (see paper 3) together with a typical value of 1.5 eV for  $\chi_G$  gives  $R$  as about 1.7 eV which is well below the carbazole triplet energy of 3 eV. However, exciplex formation should always be energetically possible since, applying the formula of Förster<sup>4</sup> to the solid state case here, the exciplex energy  $E_c$  is given approximately by:

$$E_c \approx (I_G - \chi_G) - P^+ - P^- - C = R - C \quad (2)$$

where  $C$ , the Coulomb energy of attraction between the anion and cation at their equilibrium separation in the exciplex, will always be substantial and positive so that the exciplex energy will always be less than the recombination energy. This approach also applies to the excited state of weak charge-transfer complexes since they will, by definition, show only a small degree of charge exchange in their ground states and thus to satisfy wavefunction orthogonality will have a large degree of charge donation in their excited states<sup>5</sup> just as exciplexes do. The constituent molecules will in fact be virtually ions.

In view of the foregoing considerations the main requirements for a suitable electron-accepting additive for

an electroluminescence device based on PVCz films are that it shall form an efficient fluorescent charge-transfer complex or exciplex with carbazole groups and that its electron affinity shall be reasonably high (to promote electron transfer to it from the cathode and possibly also electron hopping through the additive molecules (see paper 2) to form an electric current) but not so high as to shift the exciplex emission into the red region where non-radiative processes sharply decrease the fluorescence efficiency. The additive must also have reasonable solubility in PVCz so that it can be introduced into the polymer in substantial quantities without separating out to form inhomogeneous regions.

Study of data on fluorescent aromatic complexes indicated that some of the most fluorescent ones are those involving cyanobenzene molecules and that the fluorescence efficiency of these is promoted by the use of weak complexes, as expected, and by a rigid rather than fluid surrounding medium. In this work therefore only cyanobenzene electron acceptors were studied as additives.

## EXPERIMENTAL

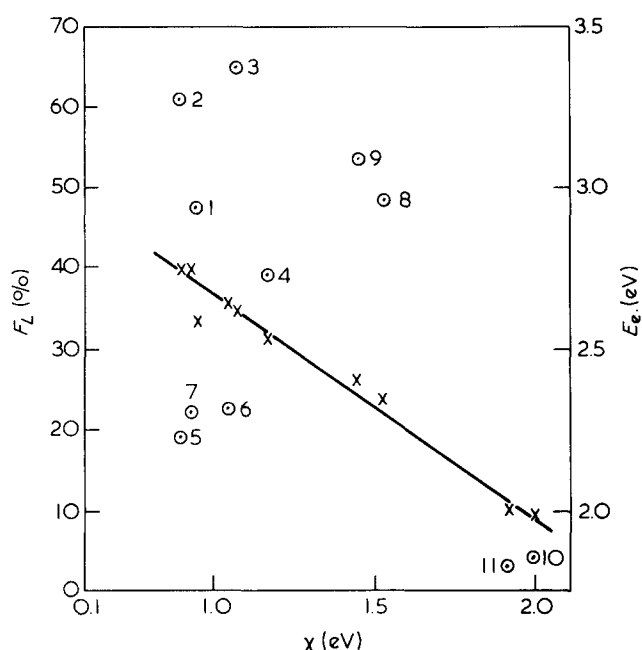
Two types of PVCz were used, one being commercial Luvican M170 obtained from BASF and purified by three precipitations from solution by methanol and the other being an Aldrich 'secondary standard' material with a known (broad) molecular weight distribution which was used as supplied. Scintillation grade tetraphenylbutadiene (TPB) was obtained from Koch Light and the three dicyanobenzene (DCNB) electron acceptors from Aldrich, none of these being purified further.

1,3,5-Tricyanobenzene (s-TriCNB) and 1,2,4,5-tetracyanobenzene (TCNB) were made by the dehydration of the corresponding amides with thionyl chloride, following Lawton and McRitchie<sup>6</sup>, and 1,2,4-tricyanobenzene (1,2,4-TriCNB) by a similar dehydration following Otten and Papenfuhs<sup>7</sup>. 2,4,6-Trimethyl-1,3,5-tricyanobenzene (s-TriMTriCNB), 2,4,6-triethyl-1,3,5-tricyanobenzene (s-TriETriCNB) and 2,4-diethyl-1,3,5-tricyanobenzene (DE(s-TriCNB)) were made by the method of Weis<sup>8</sup> by the reaction of copper cyanide and pyridine with the appropriate bromo- and alkyl-substituted benzene in a Carius tube at 200°C. 3,6-Dimethyl-1,2,4,5-tetracyanobenzene (DMTCNB) and 3,6-dimethyl-1,2,4-tricyanobenzene (DM-1,2,4-TriCNB) were synthesized by reaction of copper cyanide with tetrabromo-*p*-xylene in dimethylformamide, followed by pouring into water containing ethylenediamine<sup>9</sup>.

The film casting, by spinning or by slow evaporation of solvent, and the film thickness and electrical measurements were all done as described in paper 2.

The fluorescence emission spectra were measured with a Spex Minimate monochromator and an EMI 9558B photomultiplier and a correction was made where necessary for the variation of sensitivity with wavelength of the S20 photocathode of the photomultiplier. No such correction was made for the monochromator grating since the efficiency of this was relatively constant over the visible region. The fluorescence emission spectra of the samples were excited by an Oriel mercury-argon calibration lamp with short-wavelength filter.

Relative fluorescence intensity measurements were made by comparing the emission intensity from the



**Figure 1** Cyanobenzene electron affinity,  $\chi$ , versus photon energy of exciplex fluorescence spectrum peak,  $E_e$  (at low acceptor concentration), and maximum percentage relative fluorescence intensity of exciplex,  $F_L$ . Points: 1, 1,2-DCNB; 2, 1,3-DCNB; 3, 1,4-DCNB; 4, s-TriCNB; 5, s-TriMTricNB; 6, DE(s-TriCNB); 7, s-TriETriCNB; 8, 1,2,4-TriCNB; 9, DM-1,2,4-TriCNB; 10, TCNB; 11, DMTCNB. X, Fluorescence spectrum peak; ○, fluorescence efficiency

sample film with that from a fluorescent film standard that was made up by casting a PVCz solution containing 10 wt% of TPB onto a quartz disc. TPB is a well known scintillation material and has a fluorescence quantum efficiency approaching 100%. The fluorescence comparisons were done in a standard Perkin-Elmer 402 ultra-violet/visible spectrophotometer with the film under test in the sample beam, followed by a lens to collect as much fluorescence as possible, and the fluorescent standard plus a similar lens in the reference beam. Excitation by radiation from the monochromator of the spectrophotometer used only wavelengths that were strongly absorbed by the polymer itself so that there was negligible transmission of the exciting radiation. Stray light in the visible region, to which the PVCz samples were transparent, was estimated by replacing the sample with a non-fluorescent glass filter that absorbed in much the same region as the polymer. Stray light corrections were then made to the fluorescence results where necessary. A correction was also made for differences between the fluorescence emission spectra of the sample and the standard due to the variation in the sensitivity with wavelength of the photomultiplier.

The low-temperature cell used for absorption and thermoluminescence measurements following  $\gamma$ -irradiation at liquid-nitrogen temperature was of a standard cold finger design contained in an evacuated case holding two Spectrosil windows and fitted with a thermocouple attached to the sample mounting block. The whole cell was designed to fit into a Gammacell 220 cobalt-60  $\gamma$ -irradiation facility having a dose rate of  $320 \text{ krad h}^{-1}$ . The Perkin-Elmer 402 spectrophotometer was adapted to take the cell for the low-temperature

absorption measurements while the thermoluminescence measurements were made by simply emptying the cold finger of liquid nitrogen and allowing the cell to warm up slowly in front of the monochromator while monitoring both the thermoluminescence intensity and sample temperature.

## RESULTS

### Fluorescence of PVCz/cyanobenzene films

A range of PVCz films a few micrometres thick were prepared containing different quantities at the various available cyanobenzene electron-acceptor molecules. Films containing acceptors of relatively high electron affinity were somewhat coloured, indicating formation of stable weak charge-transfer complexes, but those containing the weakest acceptors had no perceptible extra absorption and so the complexes formed in these and responsible for their red-shifted fluorescence (relative to that of the polymer alone) may have been stable only in the excited state and thus true exciplexes. Since no clear practical demarcation exists between exciplexes and excited very weak charge-transfer complexes, the term exciplex will be used hereafter to cover both.

The photon energy at the peak of the u.v.-excited exciplex fluorescence spectrum of each film at low acceptor concentration (generally 0.5 wt% of the PVCz) is plotted in *Figure 1* against the electron affinity of the acceptor molecule. The electron affinities of five of the acceptors were taken from the compilation of Chen and Wentworth<sup>10</sup> while values for the others were obtained through measurement of the photon energy of their charge-transfer absorption peaks when each was separately complexed with an electron donor (usually pyrene or tetramethyl-*p*-phenylenediamine) in dichloromethane solution, as described in paper 1. From *Figure 1* it can be seen that the photon energy of the exciplex fluorescence changes quite smoothly with the electron affinity of the acceptor molecule, which is as expected on the basis of equation (2).

Also plotted in *Figure 1* is the maximum relative fluorescence intensity,  $F_L$ , that was observed for each acceptor (as compared with the TPB standard) after variations of acceptor concentration, PVCz material and film casting technique. Here there is no obvious trend with acceptor affinity except for the expected sharp fall for emissions extending significantly into the red region. However, a considerable degree of fluorescence intensity at room temperature is demonstrated, with a number of the exciplexes being only about a factor of 2 lower than the highly fluorescent TPB standard.

Typical variations in exciplex fluorescence intensity with acceptor concentration are shown in *Figure 2* for three different acceptors. All three curves show the same general trend of rising intensity towards a maximum with a steady decline thereafter, but a large variation in the scale of the concentration dependence is evident. Such curves were found to be sensitive in most cases to the type of PVCz used. Thus use of the 'secondary standard' PVCz generally gave more exciplex fluorescence than did commercial Luvican M170 PVCz, sometimes half as much again, with the maximum output occurring at an acceptor concentration much less than that for Luvican with some acceptors (particularly 1,3-DCNB and DM-1,2,4-TriCNB) and appreciably greater than for Luvican with other acceptors (particularly DE(s-TriCNB)).

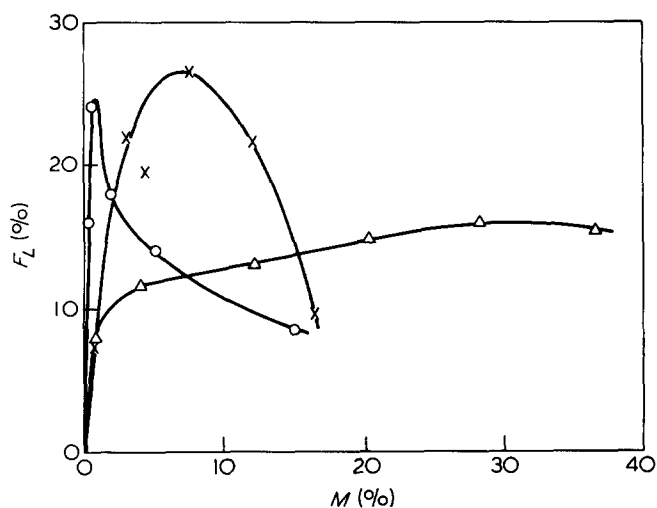


Figure 2 Percentage relative fluorescence intensity of exciplex,  $F_L$ , versus percentage molar ratio of acceptor molecules to PVCz carbazole groups,  $M$ : X, 1,2-DCNB in Luvican PVCz cast by slow solvent evaporation;  $\Delta$ , s-TriETriCNB in Luvican cast by slow solvent evaporation;  $\circ$ , 1,2,4-TriCNB in secondary standard PVCz cast by spinning. (Values have been divided by 2)

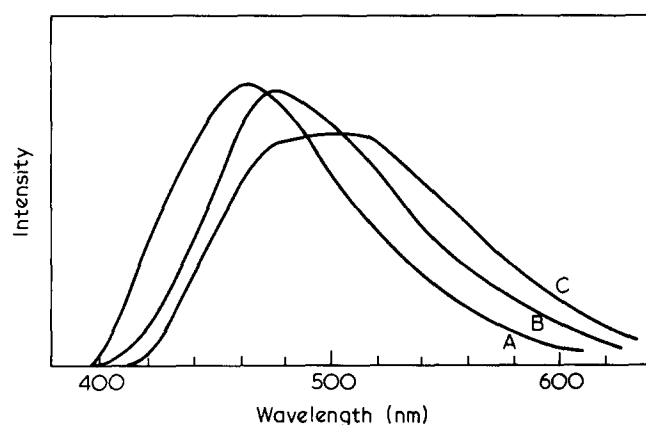


Figure 3 Fluorescence spectrum of PVCz films containing three different concentrations by weight of DE(s-TriCNB): A, 1%; B, 20%; C, 50%

Likewise spin casting of secondary standard PVCz gave for many acceptors about twice as much fluorescence as for films of similar material cast by the slow evaporation of solvent method, with in several cases a much reduced acceptor concentration at the maximum of the fluorescence intensity curve (particularly for 1,2-DCNB and 1,2,4-TriCNB). Spin casting also enabled more of each acceptor to be incorporated into a film without separating out, by up to a factor of 2 in some cases.

The fluorescence of pure PVCz has been found to come entirely from excimer sites each formed by a pair of carbazole groups in close proximity to one another. These are excited by efficient transfer of excitation energy between single carbazole groups along the polymer chains until a (lower energy) excimer site is reached<sup>11</sup>. In the presence of a small but increasing amount of electron acceptor in the PVCz film, the increasing exciplex fluorescence was found to be always matched by a decreasing amount of excimer fluorescence. Since

fluorescence excitation in the spectrophotometer was done at wavelengths below 350 nm, which is in the region of strong carbazole absorption, the bulk of the existing radiation must have been absorbed in the polymer itself initially (with the partial exception of the slightly coloured complexes formed by a few of the strongest acceptors, which may have absorbed some of the exciting radiation directly). Thus the fall in polymer excimer fluorescence and corresponding rise in exciplex fluorescence demonstrates a competition between the excimer sites and exciplex sites for the migrating singlet excitation energy. It was noticeable that films which showed increased exciplex fluorescence due to the use of different PVCz material or methods of film casting also tended to show greater polymer excimer fluorescence at comparable acceptor concentrations. This suggests that the increase in exciplex fluorescence was in this case due not so much to a high probability of excitation capture by the exciplex sites in competition with the excimer sites as to an increased extent of excitation energy migration through the polymer due to a reduction in radiationless excitation energy loss processes. This might be caused by factors such as chemical impurity content, molecular weight (e.g. fewer chain ends in high molecular weight materials), molecular weight distribution and the degree and nature of the polymer crystallinity but no detailed data were available on these.

A reason for the decline in exciplex fluorescence at higher acceptor concentrations shown in Figure 2 was suggested by a study of the exciplex fluorescence spectrum. In all cases the spectrum shifted towards the red as the acceptor concentration increased, as is shown in Figure 3 for one particular acceptor, DE(s-TriCNB), which was apparently due to the emergence of one, or sometimes two, new fluorescence spectra at the higher concentrations together with quenching of the low concentration spectrum. Figure 4 indicates the diversity

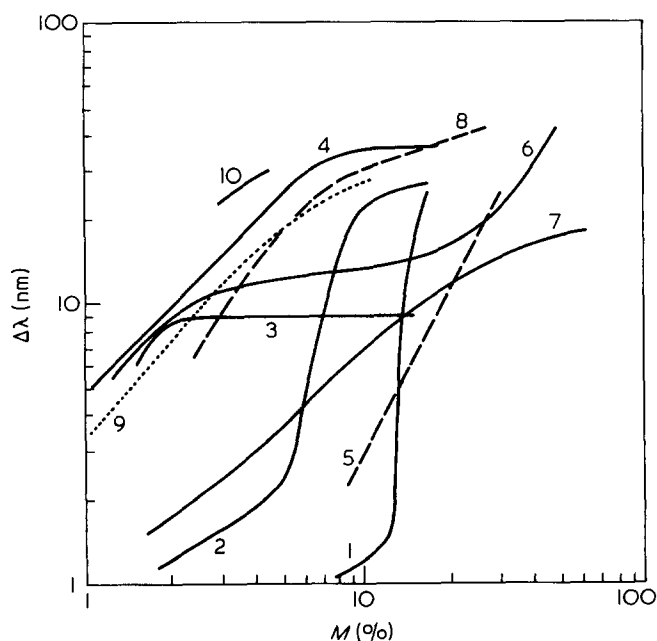


Figure 4 Shift of peak fluorescence wavelength,  $\Delta\lambda$ , with percentage molar ratio of acceptor molecules to PVCz carbazole groups,  $M$ . Acceptors numbered as in Figure 1. Some lines broken for clarity

shown by different acceptors within this general trend by plotting the amount of red-shift for each exciplex spectrum against acceptor concentration; the lines shown are smoothed results, to avoid confusion on the figure and thus do not reflect a sometimes appreciable sample-to-sample variation. The effect on this red-shift of the use of different PVCz materials and film preparation techniques was not greatly investigated but for 1,2,4-TriCNB, which was studied in the most detail and which had shown substantial variation of fluorescence intensity on this account, there was no obvious correlation.

The change of fluorescence spectrum with increasing acceptor concentration could be due to the formation of exciplexes of rather different, and less probable, conformation to those prevalent at low concentrations, since the energy of an exciplex between two dissimilar molecules will depend upon their mutual separation and orientation. However, rather more likely is that at high concentrations acceptor molecules start to add on to existing exciplex sites to form triple-molecule exciplexes or 'exterplexes'. Such exterplexes, which always fluoresce at longer wavelength than their parent exciplexes, have already been postulated<sup>12-15</sup> to explain fluorescence from mixtures of PVCz and dimethyl terephthalate (DMTP). In these cases the exterplex was assumed to consist of two donor molecules (carbazole groups) and an acceptor molecule (DMTP) arranged probably in a (DDA)\* configuration since theoretical analysis<sup>16</sup> and other evidence<sup>17</sup> suggests that this is generally more stable than a (DAD)\* configuration. By contrast the observations here of new red-shifted spectra at high acceptor concentrations suggest the presence of two acceptor molecules and just one donor to form, probably, a (DAA)\* configuration, although the extra spectrum apparently present in some PVCz/cyanobenzene films at high acceptor concentration might be a (ADA)\* configuration or perhaps even a quadruple system such as (DDAA)\* or (DAAD)\*.

The time-resolved fluorescence studies of Hoyle and Guillet<sup>13</sup> on the PVCz/DMTP system in solution at room temperature indicate that exterplex formation occurs by addition of a donor carbazole group to an existing PVCz/DMTP exciplex and/or by addition of an acceptor DMTP to an existing polymer excimer. In the solid films considered here with their limited opportunity for molecular diffusion, it seems more likely that potential exciplex and exterplex configurations are formed in the film during casting and that on excitation of the polymer there is then direct competition for the excitation between potential excimer, exciplex and exterplex sites.

The decrease in fluorescence intensity at the higher acceptor concentrations shown in *Figure 2* can be explained if it is assumed that the exterplexes usually have appreciably lower fluorescence efficiencies than their parent exciplexes. Then as the acceptor concentration increases the addition of each extra acceptor molecule to the existing exciplex sites constitutes a simultaneous creation of a new potential exterplex site and the destruction of an existing exciplex site, thus steadily increasing the ratio of the (less fluorescent) exterplexes to exciplexes and so eventually leading to a steady fall in overall fluorescence efficiency and a red-shift of the overall fluorescence spectrum. However, if the exterplex has much the same fluorescence efficiency as the exciplex it replaces then the fluorescence efficiency will remain almost constant while the spectrum red-shifts, which

appears to be the case when s-TriETriCNB is the acceptor as can be seen from *Figures 2* and *4*. There does seem, however, to be some other mechanism operative in a few cases since in the extreme example of spin cast films containing 1,2,4-TriCNB the very rapid variation of fluorescence efficiency with acceptor concentration shown in *Figure 2* is accompanied by a spectrum red-shift that is no larger than for a number of other cyanobenzene acceptors. Possibly in this case the rather different polymer structure that is apparently produced by spin casting and which seems to promote excitation migration is modified by quite small amounts of additive.

In relating all the above results to the problem of electroluminescence production it must be recalled that the basic aim remains to find an electron-accepting additive that has a substantial electron affinity and that can be added to PVCz in large concentrations to form an exciplex of considerable fluorescence efficiency. From *Figure 1* it is clear that, for the cyanobenzenes at least, the electron affinity limit will be  $\leq 1.6$  eV as the fluorescence efficiency is too low for stronger acceptors than this. From *Figure 2* it is clear that even some acceptors with affinities well below this limit will be unsuitable because their fluorescence falls off substantially as the concentration rises, due largely to exterplex formation. It would thus be desirable to find a way of inhibiting the production of exterplexes. One possible way to do this is to load PVCz with a high level of an inert filler in addition to the acceptor so as to increase the average separation of the acceptor molecules. Tests of this using the ICI product 'Cereclor 70' (a low molecular weight wax) as filler and 1,2,4-TriCNB as acceptor showed definite promise since the red-shift was substantially reduced and the fluorescence efficiency at high concentrations substantially increased as compared to samples not containing Cereclor. For instance at 20 wt% of 1,2,4-TriCNB compared with PVCz the addition of 50 wt% of Cereclor raised the fluorescence efficiency from 6% to 15%, and furthermore the Cereclor allowed about 50% more acceptor to be added to the PVCz film than would have been possible without it. However, as the Cereclor also seemed to make the film rather more liable to electrical breakdown this approach was not pursued further.

A second possible way to limit exterplex formation is via the use of inert but bulky substituents on the acceptor molecules themselves. The rationale for this is based on the theoretical calculations of Mimura *et al.*<sup>16</sup> on naphthalene/1,4-DCNB exterplexes which showed that the (DDA)\* configuration is more stable than the (DAD)\* configuration largely because of the excimer-like interaction of the two donor molecules; that is, the exterplex can to some extent be considered as an exciplex between an excimer and an acceptor. It is known that excimer formation is easily inhibited by the presence of bulky substituents on the interacting molecules because the charge resonance between the molecules which is partially responsible for the attractive force stabilizing the excimer is dependent upon the orbital overlap integral, which falls off rapidly with increasing intermolecular separation. On the other hand exciplex formation is not so sensitive to such substituents since here the interaction is basically a Coulombic one due to the charge on each molecule of the pair. Thus it might be anticipated that the presence of bulky substituents would inhibit exterplex formation through weakening of the 'excimer portion' of the (DAA)\* configuration exterplex but would not much

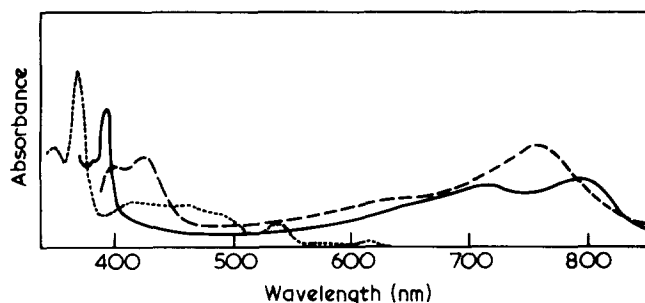


Figure 5 Absorption spectra of samples at 77K after  $\gamma$ -irradiation: — NEC in polyethylene sheet (2 mm thick); ··· s-TriCNB ( $5 \times 10^{-3}$  molar) in TPX sheet (3.5 mm thick); - - - moulded bar of PVCz (3 mm thick)

affect exciplex formation. This approach was tested by synthesizing cyanobenzenes with methyl or ethyl substituents. These substituents are chemically relatively inert but they do probably act as weak donors of charge to the  $\pi$  electron system and thus work in opposition to the electron-withdrawing cyano groups, so being at least partially responsible for the small reduction in electron affinity shown in Figure 1 as compared with the corresponding unsubstituted cyanobenzenes. The methyl group is not actually very bulky and thus a large effect would not be expected but the bigger ethyl group should be more effective. The results can best be seen from the red-shift data of Figure 4. It is clear from these that the s-TriMTriCNB, s-TriETriCNB and DE(s-TriCNB) acceptors do indeed all have red-shifts that are much smaller at equivalent molar concentrations than those of their parent unsubstituted molecules. This thus indicates inhibition of exciplex formation, with only DM-1,2,4-TriCNB which is the least heavily substituted of all, showing little change from its parent. An extra benefit of ethyl substitution is also indirectly apparent from Figure 4 in that it was found to increase the solubility of cyanobenzenes in PVCz and so enable the use of much higher acceptor concentrations. Unfortunately ethyl substitution was achieved only on s-TriCNB and this resulted in a reduction of its already fairly low electron affinity; ethyl substitution of higher affinity acceptors such as 1,2,4-TriCNB and TCNB would have been much more valuable as regards anion formation at the cathode of an electroluminescence device.

#### Ion recombination

The exciplex and excimer fluorescence described in the previous section was induced by ultra-violet radiation but in an electroluminescent device it is necessary that it should instead be induced by recombination of donor cations with acceptor anions. Such luminescent recombination processes have been observed before in chemiluminescence and electroluminescence studies in solution but it was felt advisable to seek evidence that carbazole cations and cyanobenzene anions would indeed radiatively recombine in a solid PVCz film. This was achieved by observing the thermoluminescence emission from a thick solvent-cast film of PVCz containing s-TriCNB that had been  $\gamma$ -irradiated at liquid-nitrogen temperature and then warmed. As the thermoluminescence produced in organic materials by ionizing radiation is almost invariably associated with ion recombination<sup>18</sup> and as it is often possible to observe the

'frozen' ions by ultra-violet/visible light spectroscopy before they recombine on warming, this provides a reasonably unambiguous demonstration of any radiative recombinations.

In Figure 5 is shown the absorption spectrum of a 2 mm thick sheet of polyethylene containing *N*-ethylcarbazole (NEC) that had been  $\gamma$ -irradiated at 77K with a dose of 800 krad. Since polyethylene alone under these conditions shows only a very broad featureless absorption<sup>19</sup> the observed absorption peaks at 394, 720 and 795 nm must be due to products related to NEC. The 720 and 795 nm peaks can be assigned to the NEC cation since similar absorption peaks have been observed in laser photolysis studies<sup>14,20-22</sup> of NEC and *N*-isopropylcarbazole. The 394 nm peak is at too short a wavelength to have been seen in the photolysis work. It does not seem likely to be predominantly due to the NEC anion, although there could be a small contribution from this, since while the anion does indeed absorb in this region it exhibits three closely spaced peaks<sup>23</sup> rather than one dominant one. Furthermore the anion has a second broad peak at about 680 nm which is not apparent here and also the spectrum was not affected by addition of s-TriCNB which would successfully compete with NEC for electrons. It may well therefore also be due to the NEC cation and if so is likely to be the monocarbazole cation counterpart of the prominent 430 nm peak of the carbazole dimer cation discussed extensively in paper 1.

Also shown in Figure 5 is the absorption spectrum of a PVCz moulded bar which had likewise been  $\gamma$ -irradiated at 77K and this shows peaks at about 398, 425, 640 and 760 nm. The 398 nm peak is probably the counterpart of the 394 nm NEC peak and thus can likewise be tentatively assigned as the PVCz monocarbazole cation. The 760 nm peak is also probably due to this cation since pulse radiolysis<sup>24</sup> and laser photolysis<sup>14,22</sup> measurements have found that it gives a single broad peak at around 760 nm rather than the twin peaks of the NEC cation due, apparently, to interaction of the cation with neighbouring neutral carbazole groups on the same chain. The small 425 nm peak seen in the PVCz bar but not in polyethylene containing NEC may well be due to the formation, even at this low temperature, of some carbazole dimer cation with the much larger average carbazole group separation of the latter sample inhibiting dimer formation in that case. The 640 nm peak cannot be assigned at present although it might also be a part of the monocarbazole cation absorption.

A 300 krad irradiation of a 0.4 mm thick cast film of PVCz containing 5 wt% of s-TriCNB (the largest amount that could be incorporated without the additive crystallizing out) gave a weak absorption spectrum similar to the stronger one produced by irradiation of s-TriCNB in a much thicker sheet of TPX polymer and shown in Figure 5. This spectrum is likely to be due to the s-TriCNB anion, in view of the substantial electron affinity of the parent molecule, and indeed the peak seen at 540 nm has previously been assigned to this anion<sup>25</sup>. The same PVCz sample also showed the PVC cation absorption at 760 nm and thus the presence of both PVCz cations and acceptor anions was demonstrated, as stabilized at 77K after irradiation.

To establish the occurrence of radiative recombinations between these ions some irradiated PVCz samples, both with and without s-TriCNB additive, were warmed from 77K in front of a monochromator and

photomultiplier. Thermoluminescence emission was observed from both types of sample but that from samples without additive was blue in colour and of fairly low intensity while that from samples with *s*-TriCNB was much more intense, by a factor of about 20, and yellow-green in colour as observed for the u.v.-excited fluorescence of the PVCz/*s*-TriCNB exciplex. Such exciplex emission as part of the thermoluminescence process could have resulted from the direct recombination of acceptor anions and PVCz cations, as desired for electroluminescence generation. However, it could also have come from recombination of PVCz cations with electrons trapped by the polymer (as PVCz anions) to form excited carbazole states which then migrated to the *s*-TriCNB sites to excite them. This latter process would not have been useful for electroluminescence since it involves the need to form PVCz anions, which was the purpose of adding electron acceptors to avoid. However, this second process is not likely to be important here because while the thermoluminescence output of samples with *s*-TriCNB was about 20 times higher than of samples without this additive, their fluorescence efficiency under u.v. excitation in the carbazole absorption band was only 4–5 times greater than samples without additives. Thus the extra output must have come from the trapping of extra electrons by the additive itself and the subsequent use of these in the thermoluminescence process, showing that the *s*-TriCNB was acting as an electron trap as well as, in conjunction with a carbazole group, a luminescence centre. Furthermore the thermoluminescence glow curve (plot of thermoluminescence intensity *versus* temperature during warming) was found to contain just a single peak in both cases but this peak occurred at about 155K for samples with *s*-TriCNB, for a 6K min<sup>-1</sup> warming rate, while in samples without additive it occurred at about 147K for the first 300 krad irradiation but then steadily shifted to about 182K after a series of further irradiations (due, probably, to the presence of radiation-produced electron traps such as free radicals). This also therefore indicates that addition of *s*-TriCNB creates a new electron trap which behaves differently from the traps in samples without additives. It could be, of course, that the *s*-TriCNB acts only as a trap at very low temperatures and then gives up its electrons by purely thermal activation as the temperature rises so that the electron can recombine with and excite a PVCz cation. However the 1.17 eV electron affinity of *s*-TriCNB is so far above the 0.01 eV of thermal energy available at the glow peak temperature of 155K that this can be discounted.

It is concluded therefore that *s*-TriCNB anions and PVCz cations can radiatively recombine, as required for electroluminescence generation, and the same is likely to be true for other cyanobenzene anions. The observed glow peak is likely to be initiated either by the *s*-TriCNB anions becoming mobile within the PVCz matrix at temperatures above the onset of this peak at about 100K or else, and more likely, to the PVCz cations becoming mobile at this temperature via charge hopping (see paper 2) and so migrating to the *s*-TriCNB anions.

#### Electroluminescence

During the electroluminescence studies a variety of cathode materials were used in conjunction with PVCz films doped with different cyanobenzene additives. Initial measurements were directed towards assessing whether electron injection was occurring into the film from the

cathode. The first such experiments were made with PVCz films containing about 50 wt% of 1,2,4-TriCNB onto which was vacuum evaporated a film of lithium, which has the highest work function (about 2.5 eV) of the alkali metals. Such evaporation onto a film held at about room temperature gave a mirror-like lithium film with no outward signs of chemical reaction but if the PVCz film temperature was raised, by passing a current through its conducting glass substrate, to more than 320K prior to lithium evaporation then a strong purple coloration could often be observed when the lithium film formed which was probably due to the desired electron transfer from the cathode to the cyanobenzene. Evaporation of calcium (work function about 2.9 eV) instead of lithium was also found to give a dark colour at the interface with the PVCz film, but in this case the film needed to be preheated to at least 390K. No significant colour changes were seen when magnesium (work function 3.7 eV) or aluminium (work function 4.1 eV) were used instead of lithium or calcium for these evaporations.

The current-voltage curve of a single layer PVCz film containing 55 wt% of 1,2,4-TriCNB and having a lithium cathode (without preheating of the PVCz to promote electron transfer) exhibited a current varying largely as the square of voltage, although the current was fairly erratic and dropped steeply at voltages around 1V. No electroluminescence was seen but current densities were limited to 3 A m<sup>-2</sup> by the thickness of the films (around 2 μm) and the instability of the current. Interpretation of the  $V^2$  portion of the space-charge-limited current (see paper 3) would lead to a carrier mobility value some 20 times higher than that found for PVCz alone, suggesting that either the large amount of electron acceptor added raises the mobility by reducing the extent of positive charge trapping in the polymer (see paper 2) or else, rather less likely, that an appreciable negative charge current is flowing via the electron acceptors.

Use of the two-layer film configuration used in paper 3, with a PVCz/SbCl<sub>5</sub> layer for smooth positive charge injection and a PVCz/cyanobenzene layer on top of that, brought the first observations of electroluminescence under ambient atmospheric conditions. These measurements initially used about 10 wt% of *s*-TriCNB as the additive and either barium (work function 2.5 eV) or calcium cathodes, with the cathodes being given some atmospheric protection by evaporating successive layers of aluminium, lead and more aluminium on top of them. The current-voltage curves were essentially the same 'S' shape as seen for the caesium cathode devices (paper 3) and a weak greenish-yellow electroluminescence was visible for current densities above about 100 A m<sup>-2</sup>. This electroluminescence came only from the area of film in contact with the barium or calcium cathode and not from the protective aluminium film around the edges, thus demonstrating clearly that the emission was associated with electron injection from the low work function cathode and was not due to some breakdown process dependent only upon field strength.

Following this successful two-layer structure a three-layer film configuration was investigated using a PVCz/SbCl<sub>5</sub> first layer, a PVCz with 15 wt% of 1,2,4-TriCNB second layer and an equimolar PVCz/trinitrofluorenone (TNF) third layer with an evaporated aluminium cathode. TNF is a well known electron acceptor having very good compatibility with PVCz. The combination of these materials has been extensively

investigated<sup>26</sup> due to its use as the sensitive element in xerography and as a result it is known that appreciable negative carrier currents can flow through it (via the TNF molecules) if electron injection into it is arranged<sup>27</sup>. TNF has an electron affinity of 2.17 eV<sup>10</sup> which is appreciably higher than that of the cyanobenzenes (apart from TCNB) used in this study. Tests on single-layer films indicated that aluminium was probably able to inject electrons into PVCz/TNF and it was thus hoped that field-assisted electron injection from PVCz/TNF into PVCz/1,2,4-TriCNB might be possible, leading to radiative recombinations between polymer cations and the cyanobenzene anions. However, no electroluminescence was detected for current densities up to about 10 A m<sup>-2</sup> and so it was concluded that the difference in electron affinities between TNF and 1,2,4-TriCNB was too great (about 0.64 eV) for even field-assisted electron transfer to occur.

Subsequent studies reverted to the two-layer film structure again but now using s-TriETriCNB as the electron acceptor. This acceptor had the best solubility in PVCz (but also one of the lowest electron affinities) of all the cyanobenzenes investigated and thus could be loaded into PVCz at the highest concentrations, yet as shown earlier its exciplex with PVCz had relative freedom from fluorescence quenching by weakly fluorescent exciplex formation. Use of up to 75 wt% of the acceptor together with barium or calcium cathodes gave once again the 'S' shaped current-voltage curves but this time accompanied by stronger electroluminescence than found for the much lower concentrations 1,2,4-TriCNB earlier. Emission was first visible in the dark at current densities in the range 1-6 A m<sup>-2</sup> and in one case was sufficiently bright at a current density of about 100 A m<sup>-2</sup> to be visible in indirect artificial room lighting conditions; the emission colour in this case was almost white due to the use of 5 wt% of the stronger acceptor 1,2,4-TriCNB mixed with 60% of the s-TriETriCNB. In cases where the cathode was protected by an aluminium layer there was no immediate visual change in the electroluminescence intensity or colour when the devices were transferred from vacuum to ambient atmospheric conditions. A longer-term diminution of intensity was apparent however as the cathode slowly reacted with the atmosphere. In most cases the electroluminescence was of fairly uniform intensity although in a few cases brighter spots could be seen, often associated with visible defects in the film.

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