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(54) ELECTROLUMINESCENT DEVICES AND MANUFACTURE THEREOF

ELEKTROLUMINESZIERENDE VORRICHTUNGEN UND VERFAHREN ZU IHRER HERSTELLUNG

DISPOSITIFS ELECTROLUMINESCENTS ET LEUR FABRICATION

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Description

Field of the Invention

This invention relates to electroluminescent devices and to their manufacture and particularly to such devices which have a conjugated polymer as the light emissive layer.

Background to the Invention

Electroluminescent devices of the type with which the present invention is concerned are described for example in PCT/WO90/13148. Reference may also be made to articles by Burroughes et al in Nature (1990) 347,539 and by Braun and Heeger Applied Physics Letters (1991) 58,1982.

These devices offer potential as large-area flat-panel displays since they can be fabricated over large areas using solution-processing techniques. The basic structure of these electroluminescent (EL) devices comprises a polymer film sandwiched between two electrodes, one of which injects electrons, the other of which injects holes.

In the Nature reference the importance of balancing electron and hole injection rates through selection of charge injection electrodes is recognised. For these polymers, it is clear that injection and transport of electrons is less easy to achieve than for holes; this was indicated by the demonstration of improved device efficiencies when low work function metals such as calcium were used as the negative contact layer, as explained in the article in Applied Physics Letters. From photoluminescence studies it has been identified that an important non-radiative decay channel for excitons in these polymers is by exciton diffusion to charged defects which act as quenching sites. Metal injection electrodes can provide many defect states and efficiencies can be raised substantially by introducing an additional layer between the emissive (polymer) layer and the calcium (electrode) layer. For this, a molecular semiconductor, 2-(4-biphenylyl)-5-(4-tert-butylphenyl)-1,3, 4-oxadiazole (butyl PBD) in a poly(methyl methacrylate) PMMA matrix has been used. This layer served both to prevent exciton migration to the metal contact and to enhance electron injection. In this context, reference is made to "Light-Emitting Diodes Based on Conjugated Polymers: Control of Colour and Efficiency", P.L. Burn, A.B. Holmes, A. Kraft, A.R. Brown, D.D.C. Bradley and R.H. Friend, Symposium N, MRS Fall Meeting, Boston Dec. 1991, MRS Symposium Proceedings 247, 647-654 (1992).

As described for example in PCT/WO92/03490, the contents of which are incorporated herein by reference, PPV can be chemically-modified to control its bandgap. For example, poly(2,5-dialkoxyphenylenevinylene) is red-shifted, by some 0.4eV, with respect to PPV. Copolymers of PPV and poly(2,5-dimethoxy-p-phenylenevinylene), PDMeOPV, allow fine-tuning of the band gap. Furthermore, controlled elimination of precursor leaving-groups allows both red- and blue- shifting of the gap with respect to that for PPV; the latter is achieved by interruption of conjugation along the chain by the presence of non-conjugated groups.

The present inventors have found that particular advantages are to be gained by devices having more than one layer of conjugated polymer between the electrodes. One advantage of this type of structure is that a broader spectrum of emitted radiation can be achieved as discussed in our copending Application WO94/03031, the contents of which are herein incorporated by reference.

One particularly suitable colour emission layer is a soluble conjugated polymer,poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene) MEHPPV. Similarly, poly(2-methoxy-5-(2-methylpentyloxy)-1,4-phenylenevinylene), poly(2-methoxy-5-pentyloxy-1,4-phenylenevinylene), or poly(2-methoxy-5-dodecyloxy-1,4-phenylenevinylene) can be used as colour emission layers. Another suitable layer is poly(3-dodecylthienylene). One object of the present invention is to provide a device in which these and similar layers are protected so that they can function effectively.

Summary of the Invention

According to an aspect of the present invention there is provided an electroluminescent device comprising a first charge carrier injecting layer capable of injecting positive charge carriers; a first layer of a semiconductive conjugated polymer being a soluble conjugated polymer and having a band gap selected such that when excited radiation at a predetermined wavelength is emitted; a'second charge carrier injecting layer capable of injecting negative charge carriers; means to enable an electric field to be applied across the said layers; and, arranged between the second charge carrier injecting layer and the first layer a second, barrier layer of an insoluble semiconductive conjugated polymer.

The first charge carrier injecting layer can be indium-tin oxide (ITO). The second charge carrier injecting layer is generally a substance having a low work function and which is reactive, for example comprise calcium. The insoluble polymer layer thus serves to protect the soluble polymer layer from mobile ions released by the reactive charge carrier injecting layer.

The second layer can be one which has been converted from a precursor to the conjugated polymer by thermal

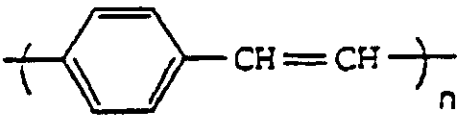
conversion.

Other ways of providing a barrier layer of a conjugated polymer includes solution or melt processing or vapour phase deposition. Another way is to put down a polymer layer and render it insoluble and intractable by a cross linking reaction carried out in situ.

The second polymer layer can also be capable of emitting radiation and the thicknesses of the first and second layers can be selected so that parts of them at least lie within an emission zone of the device, whereby radiation is emitted from both of the layers. The term "conjugated polymer" used herein indicates a polymer for which the main chain is either fully conjugated, possessing extended pi molecular orbitals along the length of the chain, or else is substantially conjugated, but with interruptions to conjugation at various positions, either random or regular, along the main chain. It includes within its scope homopolymers and copolymers. The present invention can utilise any combination of conjugated polymers capable of forming a thin electroluminescent film.

Particularly preferred conjugated polymers include poly(p-phenylene vinylene)PPV and copolymers including that polymer. Preferred features of the polymers used with the respective layers are that they should be stable to oxygen, moisture and to exposure to elevated temperatures, they should have good adhesion to an underlying layer, good resistance to thermally-induced and stress-induced cracking, good resistance to shrinkage, swelling, re-crystallisation or other morphological changes. Moreover, the polymer film should be resilient to ion/atomic migration processes, for example by virtue of a high crystallinity and high melting temperature. Particularly preferred polymers are discussed in the literature referred to above, particularly in PCT/WO90/13148 the contents of which are herein incorporated by reference.

The film of conjugated polymer is preferably a film of a poly(p-phenylenevinylene) [PPV] of formula

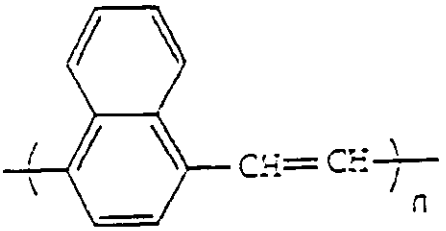


wherein the phenylene ring may optionally carry one or more substituents each independently selected from alkyl (preferably methyl), alkoxy (preferably methoxy or ethoxy), or halogen (preferably chlorine or bromine).

Any poly(arylenevinylene) including substituted derivatives thereof or any poly(arylene) is also suitable. Throughout this specification the term "arylene" is intended to include in its scope all types of arylenes including hetero-arylenes as well as arylenes incorporating more than one ring structure including fused ring structures.

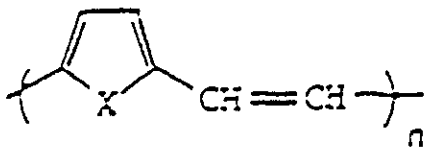
Other conjugated polymers derived from poly(p-phenylenevinylene) are also suitable for use as the polymer film in the EL devices of the present invention. Typical examples of such derivatives are polymers derived by:

(i) replacing the phenylene ring in poly(p-phenylenevinylene) with a fused ring system, e.g. replacing the phenylene ring with an anthracene or naphthalene ring system to give structures such as:-



These alternative ring systems may also carry one or more substitutes of the type described above in relation to the phenylene ring.

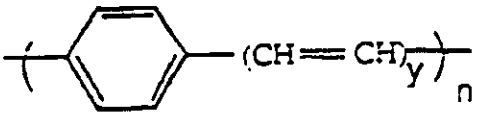
(ii) replacing the phenylene ring with a heterocyclic ring system such as a furan or thiophene ring to give structures such as:-

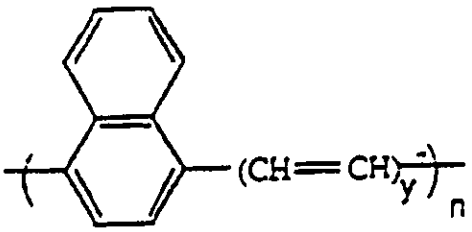


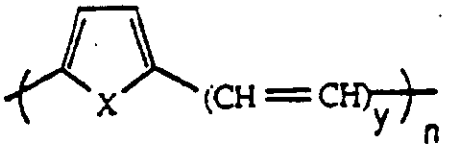
X = O, S

As before, the heterocyclic ring may carry one or more substituents of the type described above in relation to phenylene rings.

(iii) increasing the number of vinylene moieties associated with each phenylene ring (or each of the other alternative ring systems described above in (i) and (ii)) to give structures such as:-







X = O, S

where y represents 2,3,4,5,6,7, ...

Once again, the ring systems may carry the various substituents described above.

These various different PPV derivatives will possess different semiconductor energy gaps.

Other polymers which are particularly suitable for use in the present invention are the semiconductive copolymers discussed in PCT/WO92/03490, the contents of which are herein incorporated by reference. In a preferred embodiment, the copolymer is a conjugated poly(arylenevinylene) copolymer with a proportion of the vinylic groups of the copolymer saturated by the inclusion of a modified group substantially stable to elimination during formation of a film of the co-polymer. The proportion of saturated vinylic groups controls the extent of conjugation and thus modulates the semi-conductor bandgap of the copolymer.

Preferably polymers for use in the present invention are capable of being processed either as precursors which are subsequently converted to a conjugated form or as intrinsically soluble polymers. Some of the polymers referred to herein are electroluminescent and can be selected for the first layer. Others do not have electroluminescent properties but are suitable for the second barrier layer.

In the preferred embodiment, the soluble conjugated polymer layer is a poly(2,5-dialkoxyphenylenevinylene), for example poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene), MEHPPV and the insoluble polymer layer is a copolymer prepared from a precursor copolymer to PPV and poly(2,5-dimethoxy-p-phenylenevinylene), PDMeOPV. The insoluble polymer layer can be PPV.

In one preferred embodiment, there is a third layer between the soluble layer and the insoluble layer of poly(p-phenylenevinylene), PPV, which is processed from a tetrahydrothiophenium (THT)-leaving precursor polymer. With the thicknesses selected appropriately, all three layers can be caused to emit light. In a further embodiment, there is a fourth layer of an insoluble conjugated polymer converted from a precursor adjacent the first charge carrier injecting layer. The conversion of the precursor to the conjugated polymer in the second layer releases acid(H+ ions), and the fourth polymer layer adjacent the charge injecting layer serves to shield the charge carrier injecting layer from chemical attack by these H+ ions. The fourth polymer layer adjacent the positive charge carrier injecting layer can be either inert or carry intercepting functional groups (for example methoxy-substituted precursor polymer to PPV, dimethoxy-PPV, dimethyl-PPV, polyaniline and derivatives, polyvinylcarbazole, blends of dimethyl-PPV and other higher band gap polymers) to assist in the transport of positive charge carriers to the emission zone.

According to another aspect of the present invention there is provided a method of making an electroluminescent device comprising the following steps;

providing a first charge carrier injecting layer for injecting positive charge carriers;
depositing onto said charge carrier injecting layer a first layer of a soluble polymer in a solution of a first solvent;
depositing a second layer in the form of a precursor in a solution of a second solvent;
heat treating the device so that the precursor is converted to its polymer which is insoluble; and
depositing a second charge carrier injecting layer for injecting negative charge carriers.

According to another aspect of the present invention there is provided a method of making an electroluminescent device comprising the following steps:

providing a first charge carrier injecting layer for injecting positive charge carriers;
depositing onto said first charge carrier injecting layer at least one layer of a soluble semiconductive conjugated polymer which has a band gap selected so that when excited it emits radiation;
depositing a barrier layer onto the, or the last one of the, soluble polymer layers, said barrier layer comprising an insoluble and intractable semiconductive conjugated polymer;
and depositing onto said barrier layer a second charge carrier injecting layer for injecting negative charge carriers.

The invention also envisages devices made by either one of the above defined methods.

The inventors have found, surprisingly, that full conversion of the precursor-route polymer on top of a much less robust layer of soluble polymer can be achieved without damaging the soluble polymer. At the preferred temperatures for thermal conversion of 200°C, it would normally be expected that the soluble polymer layer would melt or soften.

The soluble polymer is selected so that it is soluble in the first solvent but not in the second solvent and the precursor to the polymer is selected so that it is soluble in the second solvent and not in the first solvent.

This enables the method of the present invention to be utilised to construct a multilayer device.

In one embodiment, there is a further step of putting down a third layer of a precursor after the second layer has dried. The heat treatment step is then carried out to convert the precursors of the second and third layers to their conjugated polymer.

Preferably the step of laying down the polymer and the precursor(s) is done by spin coating.

Multilayer electroluminescent devices of the type with which the present invention is concerned have strength, mechanical rigidity, stability at high temperatures and resistance to diffusion or migration of ions which are released on conversion of the precursor to the polymer. At the same time, desirable properties of the soluble polymer, such as its desirable colour or high efficiency for luminescence can be exploited.

In the preferred embodiments, the soluble polymer is a poly(2,5-dialkoxyphenylenevinylene). Examples are MEHPPV, poly(2-methoxy-5-(2-methylpentyloxy)-1,4-phenylenevinylene), poly(2-methoxy-5-pentyloxy-1,4-phenylenevinylene), and poly(2-methoxy-5-dodecyloxy-1,4-phenylenevinylene), or other poly(2,5-dialkoxyphenylenevinylenes) with at least one of the alkoxy groups being a long solubilising alkoxy group, linear or branched. Other suitable soluble conjugated polymers can also be selected from the poly(alkylthienylene)s. One example is poly(3-dodecylthienylene).

In the present invention, the soluble polymer is protected on its one side to the second charge carrier injecting layer which injects negative charge carriers. Preferably, the soluble polymer is protected on both sides by an insoluble polymer layer which has been converted from respective precursors.

The invention thus envisages fabrication of an electroluminescent device in which different solubilities of polymers and/or precursors in different solvents allows deposition of a layer of polymer onto an underlying layer. Thus, a PPV precursor polymer layer is spin coated on top of a layer of MEHPPV in one embodiment. The precursor polymer is in a solution of methanol which is not a solvent for MEHPPV, which itself is deposited from chloroform solution. As an alternative to methanol, water could be used. As an alternative for chloroform, halogenated hydrocarbons such as dichloromethane or ethers such as tetrahydrofuran could be used. As a further alternative, ketones preferably cyclohex-

anone could be used.

For a better understanding of the present invention and to show how the same may be carried into effect, reference will now be made by way of example to the accompanying drawings.

Brief description of the drawings

Figures 1a, 1b and 1c show the chemical structures of a) PPV, b) a copolymer of PPV and PDMeOPV, c) MEHPPV;
Figure 2a shows the current density against electric field characteristics of each of four devies on a log-log scale;
Figure 2b shows current density against voltage on a linear scale;
Figures 3a to 3d show diagrammatically the structures of four electroluminescent devices I to IV; and
Figure 4 shows the electroluminescent emission spectra (all normalised to a peak emission of 1 and offset) of (a) sample I, (b) sample II, (c) sample III, (d) sample IV, (e) a unilayer copolymer electroluminescent device, (f) a unilayer PPV electroluminescent device, (g) to (i) the absorption spectra of the polymers a,b, and c themselves. Curve g corresponds to polymer c) MEHPPV; curve h corresponds to polymer a) and curve i corresponds to co-polymer b).

Description of the preferred embodiments

Three different semiconducting poly(arylenevinylene)s are used to demonstrate the invention.

(a) (Figure 1a) Poly(p-phenylenevinylene), PPV, was processed from a tetrahydrothiophenium (THT)-leaving precursor polymer which is soluble in methanol, PPV has a π - π^* band gap of about 2.5eV.
(b) (Figure 1b) A copolymer was prepared from a statistical precursor copolymer to PPV and poly(2,5-dimethoxy-p-phenylenevinylene), PDMeOPV, which is soluble in methanol. The monomer feed ratio was 9:1. The synthesis of such a copolymer is described for example in a paper entitled "LEDs based on Conjugated Polymers: Control of Colour and Efficiency by P. Burn, et al given at MRS Boston 1991 and published in Mat. Res. Soc. Symp. 1992 247, 647-654. Under the experimental conditions used here, the band gap of the polymer obtained after thermal conversion is blue-shifted with respect to PPV due to the presence of non-eliminated methoxy groups at the vinylic carbons adjacent to the dialkoxy-substituted phenylenes. The resulting copolymer has a π - π^* band gap of about 2.6eV.
(c) (Figure 1c) The third polymer used was poly(2-methoxy-5-(2-ethylhexloxy)-1,4-phenylenevinylene), MEHPPV. Due to the long alkyl side-groups this derivative of PPV is soluble in and processed from chloroform. It has a π - π^* band gap of about 2.2eV.

Both the THT-leaving group precursors to PPV and the copolymer are such they can be laid down by spin coating in solution of a solvent, which when dry, forms a stable layer onto which a further layer may be put down. This enables the construction of multilayer structures since, once a layer has dried, subsequent deposition of additional polymer layers will not remove the initial layer. The two THT-leaving group precursor polymers are insoluble in chloroform, but soluble in methanol. MEHPPV is soluble in chloroform, but insoluble in methanol. This difference in solvents allows a layer of precursor to be spin-coated on top of a layer of MEHPPV without removal of the MEHPPV and vice-versa. Hence multilayer structures composed of the three different polymers were fabricated.

The multilayer devices of conjugated polymers were constructed as follows. Indium-tin oxide (ITO)-coated glass substrates were thoroughly cleaned with acetone and subsequently with propan-2-ol, both in an ultrasonic bath. Multilayer structures were formed by spin-coating layers of polymer or precursor, one on top of another as discussed above. All layers were spin-coated within a nitrogen-filled glovebox (O_2 and H_2O content 10ppm), in which all subsequent processing steps were also performed. Film thicknesses of the polymer layers were set by control of both spin-speed and solution concentration as follows: the copolymer at 20nm, MEHPPV at 50nm and PPV at more than 50nm. The thicknesses of the individual polymer layers and total polymer layer were measured with a Dektak IIA surface profiler. The samples were thermally converted at 200°C in vacuo (10^{-6} torr) for 12 hours to convert the precursor polymers. Calcium contacts were vacuum deposited on the samples and the samples were hermetically sealed. Sample areas were 1 mm^2. Four multilayer device structures have been studied here; details of construction are summarised in table 1 and illustrated in Figures 3a to 3d.

To form device I illustrated in Figure 3a, an Indium-tin oxide coated glass substrate 1 was spin coated firstly with a precursor to the copolymer (b) at a thickness of 20nm (layer 21). The layer was allowed to dry and then a precursor to PPV (a) in the thickness of 230nm (layer 22) was laid down by spin coating, and allowed to dry. Finally a layer 23 of MEHPPV (c) in the thickness of 50nm was laid down by spin coating. Layers 21 and 22 were put down in a solution of methanol and layer 23 was put down in a solution of chloroform. The sample was then heat treated to cause thermal conversion of the precursors to the copolymer in layer 21 and to PPV in layer 22. Finally a calcium contact 2 was

vacuum deposited on layer 23.

Device II as illustrated in Figure 3b was formed as follows. Onto an indium-tin oxide coated glass substrate 1 there was spin coated a first layer 31 of MEHPPV in the thickness of 50nm which was allowed to dry, and then a precursor to PPV 32 in the thickness of 50nm and allowed to dry. Then a precursor to the copolymer 33 was laid down by spin coating in the thickness of 20nm. The first layer 31 was put down in a solution of chloroform and the second and third layers 32,33 were put down in a solution of methanol. The device was heat treated to thermally convert the precursors in layers 32 and 33 to the respective polymers PPV and the copolymer and a calcium contact 2 was then vacuum deposited onto layer 33.

Device III illustrated in Figure 3c was formed as follows. Onto an indium-tin oxide coated glass substrate 1 was spin coated a first layer 41 of a precursor to the copolymer in a thickness of 20nm. The precursor was allowed to dry. A second layer 42 of MEHPPV is laid down by spin coating in the thickness of 50nm and allowed to dry and then a third layer 43 of the precursor to PPV is laid down by spin coating in a thickness of 150nm. After this layer had dried a fourth layer 44 of a precursor to the copolymer was laid down by spin coating in a thickness of 20nm. The device was then heat treated to thermally convert the precursors to their respective conjugated polymers and a calcium contact 2 was vacuum deposited onto layer 44.

Device IV illustrated in Figure 3d was formed as follows. Onto an indium-tin oxide coated glass substrate was spin coated a precursor to the copolymer 51 in the thickness of 20nm. This was then allowed to dry. A precursor to PPV 52 was laid down by spin coating in a thickness of 30nm and allowed to dry and then a precursor to the copolymer 53 was laid down by spin coating in the thickness of 20nm. The sample was then heat treated and a calcium contact 2 was vacuum deposited onto the third layer 53.

In these structures, the calcium contact 2 serves as a cathode for injecting negative charge carriers and the indium-tin oxide serves as an anode for injecting positive charge carriers. Reference numeral 4 indicates a negative contact and reference numeral 6 indicates a positive contact.

In devices II, III and IV the layer adjacent the calcium contact 2 is a layer of the copolymer which, after heat treatment, is insoluble in common solvents. This layer acts as a barrier layer to shield the cathode from chemical attack, while allowing the injection of charge carrier into the emissive region. This layer of copolymer also serves to resist the diffusion of mobile ions released from the reactive cathode through the polymer layer. It also provides the device with strength, mechanical rigidity and stability at high temperatures. Furthermore, it protects the soluble polymer (MEHPPV) so that the desirable properties of MEHPPV such as the required colour or high efficiency for luminescence can be exploited. Other conjugated polymers or other polymers which can be used as barrier layers instead of that illustrated in Figure 1b are methoxy-substituted precursor polymers to PPV, dimethoxy-PPV, dimethyl-PPV, polyaniline and derivatives, polyvinylcarbazole, blends of dimethyl-PPV and any other higher band gap polymers.

As explained above, the indium-tin oxide coated glass substrate serves as an anode for the device while the calcium contact 2 serves as a cathode. These constitute means for enabling an electric field to be applied across the layers.

The devices were driven by applying a positive bias to the ITO with a Keithley 230 voltage source and electric currents were monitored with a Keithley 195A multimeter. Electroluminescence (EL) was observed through the ITO substrate. Integrated light output was monitored with a large-area calibrated silicon photodiode in photoamperic mode, measuring the photocurrent as a voltage across a 1MΩ resistor. Spectrally-resolved EL measurements were made using a Coderg PH1 double monochromator and a Hamamatsu R943-02 photomultiplier tube. Internal quantum efficiencies, defined here as photons generated per injected charge, were measured at a device brightness of about 5cd/m^2. In calculating the internal quantum efficiency account has been taken of the effects of refraction by the glass substrate, as discussed in an article in the 1992 issue of Synthetic Metals authored by Brown, et al. UV/vis absorption spectra were recorded with a Perkin Elmer λ9 spectrophotometer on samples of polymer spin-coated on silica substrates.

The four device configurations show colours of emission from red to yellow/green. Electrical and electro-optical characteristics for these devices are shown in Table 1, and in Figures 2a, 2b and 4. In Table 1 the layers are numbered in numerical order beginning from the indium tin oxide 1. In Figures 2a and 2b note that different thicknesses of the combined polymer layers give different drive voltages, but that these scale to give a universal curve for current density versus electric field. Figure 2b shows the current density against electric field voltage characteristics of the four devices. Figure 4 shows the emission spectra from the various devices (the spectra are offset and normalised to give equal peak heights at the peak emission wavelengths). Also displayed are emission spectra from unilayer devices of PPV and the copolymer. The absorption spectra of the 3 polymers are also shown (curves g,h,i) (normalised to give a peak π - π^* absorption coefficient of 1), showing the differing optical band gaps.

Figures 2a and 2b show clearly that the current density under forward bias is determined primarily by the electric field (calculated as the applied voltage divided by the sum of the individual layer thicknesses). In contrast to the results obtained for the devices formed with PPV and the butyl PBD/PMMA layers referred to in the reference above by P.L. Burn et al, the devices studied here do not show a large build-up of space charge at the interfaces between polymer

layers. Also, the small differences in band gap for the polymers in contact with the metal electrode layers do not affect significantly the threshold fields for charge injection.

The various structures give a range of different emission colours, and by analysing these it can be identified which of the polymer layers are acting as sites for radiative decay of excitons:

Structure I was the only structure to show an emission spectrum characteristic of a single polymer layer, in this case MEHPPV. There is no contribution to the emission spectrum from excitons decaying in the PPV or copolymer layers, since at energies about 2.35eV there is no emission, whereas the emission spectra of PPV and copolymer both have strong emission intensities at 2.35eV. Probably therefore electron injection is the limiting process in the devices, so that electron and holes meet in a recombination zone adjacent to the electron-injecting calcium contact 2. It is unfavourable for the excitons formed in the MEHPPV layer to migrate into the other polymer layers which have larger band gaps. By the same argument, the absence of any contribution to the emission spectra from the PPV layer indicates that no electron-hole capture occurs in this layer and thus that no electrons migrate into the PPV layer through the MEHPPV layer, under the influence of the electric field. The copolymer and PPV layers are acting as hole transport layers. The emission spectra also demonstrate that, surprisingly, the thermal conversion process does not damage or alter the MEHPPV.

Structure II has the same combination of polymer layers as structure I but constructed the other way up. The emission spectrum of the device is broad with emission stretching from below 1.55eV to above 2.5eV. At 1.75eV, both PPV and copolymer have negligible emission yet the emission of sample II is still more than 15% of the peak emission and must be due to the radiative decay of excitons located in the MEHPPV layer. Similarly, at 2.35eV MEHPPV has zero emission, yet the emission of sample II is still more than 30% of the peak emission for the sample and so the emission at this energy must be due to the decay of excitons located in either the copolymer or PPV layers. This device is thus clearly an example of a conjugated polymer device emitting from more than one polymer layer. The nature of the generation of the excitons in the various polymer layers will be discussed later.

Structure III has an emission spectrum very similar to that for structure II. Thus the emission of this device, for the same reasons as discussed above, has contributions from the decay of excitons located in the MEHPPV layer and at least one of either the PPV or the copolymer layers. It appears the additional copolymer layer has negligible effect on the emission spectrum, and one might deduce that no excitons indeed are located in this additional copolymer layer adjacent to the ITO. This device also is an example where exciton decay occurs within the bulk of a polymer multilayer device as the MEHPPV is separated from both contacts by other layers.

Structure IV has an emission spectrum with contributions from both the PPV layer and the copolymer layer. The emission spectrum shows phonon structure at 2.07, 2.26 and 2.39eV which is less pronounced than that for PPV, though clearer than in the copolymer.

These devices operate by electron and hole injection at negative and positive electrodes, with electron-hole capture to form excitons, which can then decay radiatively. There are no large changes in the current density-electric field characteristics accompanying the introduction of several layers of polymer, so there is probably little or no charge confinement resulting in space charge build-up at the interfaces between these layers. Thus there is little modification of the internal electric field and the conditions for charge injection and charge migration are not much affected by the presence of several layers of polymer with similar band gaps.

In structures II-IV emission in several polymer layers can be observed with an emission zone more than 50nm in total thickness. It is of interest to identify the mobile species which gives rise to this wide emission zone. The two candidate mobile species are (i) charge carriers and (ii) neutral excitons. Depending on the behaviour of these charged and neutral species, we can expect to see behavious ranging from the limit where a broad electron-hole capture zone is narrow, but in which exciton diffusion acts to produce a broad emission zone.

Thus, the precise thicknesses and arrangement of the layers of conjugated polymer within an electroluminescent device can be ascertained from a knowledge of the polymer band gap, electron-hole mobilities in the polymer, and a value for the excitation diffusion lifetime with reference to the models discussed herein. Firstly these cases are outlined by two simple models to give estimates of the widths produced by the two mechanisms.

(i) Width of electron-hole capture zone.

Let us consider that electron hole capture is mediated by Coulombic attraction and will occur within a sphere of radius, $r_{capture}$, where this attraction exceeds the thermal energy. Then

$$kT = \frac{e^2}{4\pi\varepsilon_0\varepsilon_r r_{capture}}$$

$$\therefore r_{capture} = \frac{e^2}{4\pi\varepsilon_0\varepsilon_r kT}$$

Taking a value for the relative permittivity ε_r of about 4, we have at room temperature $r_{capture} \approx 14$nm. It can be demonstrated from simple models for the drift of charges through the device that, in the absence of barriers for carrier transport at interfaces, the space charge densities of positive and negative charge carriers are low, and that the width of the electron-hole capture zone can be modelled to lie in the range of the polymer layer thicknesses used for example II to IV. At an electric field, F, with a current density, j, and a carrier mobility, μ, the carrier density, p is given by

$$p = j/ev = j/eF\mu$$

Taking typical device operation values of j = 1 mA/cm^2, and F = 10^8 V/m and assuming a mobility, μ - 10^{-4}cm^2/V sec, as has been observed in similar conjugated polymers for the majority, p-type carriers gives a carrier density, p = 6.2 x 10^{20}m^{-3}. This gives a carrier-carrier separation of about 120 nm.

If electrons have a mobility, μ_n, the number of collisions an electron undergoes in time, t, is $tF(\mu_n+\mu_p)p\sigma$ where σ is the collision cross-section. Assuming every collision results in capture, we can then estimate an electron-hole capture zone width, $W_{e\text{-}h}$ given by

$$W_{e\text{-}h} = \frac{\mu_n}{(\mu_n+\mu_p)\,p\sigma} = \frac{\mu_n\mu_p eF}{(\mu_n+\mu_p)\,j\sigma} = \frac{\mu_n}{(\mu_n+\mu_p)\,p r_{capture}^2}$$

Using the values here, based on the hole mobilities estimated above, and assuming equal electron and hole mobilities, we find a value of $W_{e\text{-}h} \approx 4000$ nm. This width is very much larger than we find here, and we consider that confinement to much smaller thicknesses near the cathode results from a much lower electron mobility.

(ii) Exciton diffusion length.

We may assume a simple exciton diffusion equation, with a characteristic variance of the displacement from the origin, $1^2 \sim D\tau$. Exciton lifetimes, τ, of above 0.25 ns have been measured in PPV. Typical values of the magnitude of diffusion coefficients, D, in molecular semiconductors are of the order 1 x 10^{-3} cm^{2}s^{-1} and the coefficient in these conjugated polymers does not exceed this. These values then give an estimate of the diffusion length of an exciton, $1, \sim 5$ nm.

Although the multilayer emission is observed only in structures II-IV, it is constructive to consider an analysis of structure I first. As the emission spectrum of structure I is characteristic of the single polymer layer of MEHPPV, the recombination zone is probably confined within the 50 nm thickness of the MEHPPV layer. From the above analysis, such a zone thickness would only be consistent with electron-hole capture by a Coulomb interaction if the electron mobility is less than 10^{-6}cm^2/V sec. This may be the case, since minority carrier mobilities in organic semiconductors are often significantly smaller than those of the majority carriers. Another explanation is that there is a barrier against electron migration from the MEHPPV layer into the PPV layer and so confining the recombination zone to the MEHPPV layer.

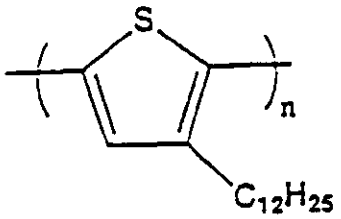
As has already been indicated, in structures II-IV the spectral shifts indicate that emission occurs in layers not solely adjacent to the calcium contact. In the scenario in which the width of the emissive layer is determined by the width of the electron-hole capture zone, there is no barrier against electron migration in all these structures since electrons pass from PPV into MEHPPV. The electron-hole capture zone then extends through several polymer layers and over more than 200 nm in structure III. Excitons are then formed in several different polymer layers and then radiatively decay in several polymer layers, given the observed emission spectra. Thus, in structure I the recombination zone is within 50 nm of the electron-injecting contact, observing emission from only one layer. The recombination zone is probably limited in this structure due to a barrier against electron migration out of the MEHPPV layer.

Though the inventors consider that the width of the characteristic emissive zone in these EL devices is in part determined by the statistics for electron-hole capture, there are other possible explanations. One such is that the recombination could be occurring within a 50 nm zone adjacent to the calcium contact (as in structure I) and that there

is subsequent exciton transfer from the recombination zone to different emission zones. This transfer could occur by several mechanisms. Firstly, there may be absorption and re-emission at a longer wavelength, but this is not significant for the devices studied here. One reason for this is that one would expect to see a concomitant fall-off in device efficiency, given that luminescence yields are not 100%. Experimentally, there is little variation in efficiency from one device to another, as summarised in Table 1.

Secondly, there may be exciton diffusion from one layer to another. The radiative lifetimes for singlet excitons in PPV are of the order of 1 nsec. Measured photoluminescence lifetimes are lower, indicating that there are competing non-radiative decay mechanisms, but lifetimes are 250 psecs or longer at room temperature, and this allows for diffusion of the exciton through the polymer prior to decay. Evidence for migration of excitons, created by photoexcitation, within a film of PPV, is provided by comparison of absorption and photoluminescence spectra. Even in polymer samples that show a considerable spread in intra-chain conjugation length, and hence band gap, such that the phonon structure expected in the absorption spectrum is washed out, the luminescence spectra show clear vibronic structure, indicating that the excitons so formed, prior to emission, have migrated to the chain segments with longest uninterrupted conjugation length and hence with lower band gap. Exciton diffusion is very well studied in molecular semiconductors and under the conditions in these conjugated polymer films may occur either by direct hopping or by Förster transfer. Energy transfer to a chromophore with a longer wavelength of emission, which can be selectively introduced as a dopant in the semiconductor, is a well-studied phenomenon.

A further example of the invention is discussed below. A different soluble conjugated polymer is used in place of the MEH-PPV. The polymer used is poly(3-dodecylthienylene), P3DT, for which the chemical structure is



This polymer is soluble by virtue of the dodecyl side-chain, and is processed from solution, in for example, chloroform. It shows good photoluminescence and has been shown to function in an electroluminescent device.

A device was fabricated in a similar manner to Example II, with a layer of P3DT (thickness 500 nm) on the ITO contact 1, and a layer of PPV precursor spin-coated on top and subsequently heated to convert to PPV (200°C, 12 hours) in place of the two precursor-route layers in Example II. Calcium was evaporated onto this as a final stage.

This device shows a high threshold voltage for charge injection, requiring 80 V or more to give readily visible emission. This high drive voltage is due to the considerable thickness of the P3DT layer. The quantum efficiency for this device was found to be about 0.08%.

The light output was observed by eye to be deep red, characteristic of the luminescence of P3DT which is considerably to the red of PPV. Emission from the PPV layer viewed through the P3DT layer and the ITO/glass substrate would be strongly attenuated by the absorption of the PPV emission by the P3DT (the PPV emission falls in the absorption band of P3DT since this has a lower band gap).

This device demonstrates various points:

(i) Emission is produced in a layer not immediately adjacent to the cathode. It can reasonably be expected that emission was also observed from the PPV layer, (c.f Example II). This is therefore another example of a multilayer emitting device, but should optimally be modified so that the polymer layer thicknesses avoid the problem of absorption by one layer of the light produced by another.

(ii) Furthermore, it is a device where a layer of precursor polymer has successfully been laid down onto a soluble polymer layer, taking advantage of the different solubilities of the polymers, and where the structure survives the thermal treatment required to convert to the conjugated form.

In summary, the inventors have discovered that multilayer electroluminescent devices with emission from more than one layer can be fabricated. Such multilayer structures could be used to control device characteristics in a range of applications. For example at least two polymer layers can be arranged to be simultaneously luminescing. This will allow generation of a broader spectrum than can be achieved with a single layer (see structures II, III and IV), and may allow fabrication of a white-light source.

A particularly important discovery is that the region of the device in which the emission occurs can be arranged to

be sufficiently wide so that several polymer layers can simultaneously emit. The probable reasons for this are firstly, that in the absence of charge trapping at an interface between two polymer layers, the electron-hole capture process requires thicknesses of polymer of at least 50 nanometers so that excitons are formed in the region of this thickness. Secondly, excitons once formed will diffuse before they decay and this process of diffusion can further broaden the width of the emission zone. The inventors have determined that for optimum performance the device should be manufactured so as to take into account the following points. As is evident from the examples, the emission is usually to be seen from the region of the polymer adjacent the cathode. This indicates that either electron injection is more difficult than hole injection and/or that electrons have lower mobility than holes. Emission from more than one layer is therefore more likely to be achieved in devices where appropriate layers are deposited close to the cathode. Another determinitive feature is the band gap of the polymer layers. Inappropriate ordering of the polymer layers can result in complete trapping of excitons within one layer only as seen in Example 1 in which there is a low band gap polymer (MEHPPV) adjacent the cathode. Thus, preferably, the band gaps are ordered to assist charge carrier transfer and capture.

Table 1.

Characteristics of the four multilayer electroluminescent devices. Polymer layer 1 was spin-coated directly on top of the ITO contact. The calcium contact was evaporated on top of polymer layer 3 (or polymer layer 4 in the case of device III).

Sample Number	I	II	III	IV
Layer 1 thickness (nm)	copolymer 20	MEHPPV 50	copolymer 20	copolymer 20
Layer 2 thickness (nm)	PPV 230	PPV 50	MEHPPV 50	PPV 30
Layer 3 thickness (nm)	MEHPPV 50	copolymer 20	PPV 150	copolymer 20
Layer 4 thickness (nm)			copolymer 20	
Colour of light emission	red	orange	orange	yellow
Quantum efficiency, η (%)	0.30	0.22	0.24	0.16
Electric field (V/cm) required to produce:				
1 mA cm^{-2}	8.0×10^5	7.1×10^5	7.4×10^5	7.1×10^5
2 mA cm^{-2}	8.6×10^5	7.7×10^5	7.9×10^5	7.7×10^5

Claims

1. An electroluminescent device comprising:

   a first charge carrier injecting layer (1) capable of injecting positive charge carriers;
   a first layer (31;42) of a semiconductive conjugated polymer being a soluble conjugated polymer and having a band gap selected such that when excited, radiation at a predetermined wavelength is emitted;
   a second charge carrier injecting layer (2) capable of injecting negative charge carriers;
   means to enable an electric field to be applied across the said layers;

   characterised in that the device comprises, arranged between the second charge carrier injecting layer and the first layer, a second, barrier layer (33;44;53) of an insoluble semiconductive conjugated polymer.

2. An electroluminescent device as claimed in claim 1 wherein the first charge carrier injecting layer (1) is indium tin

oxide (ITO).

3. An electroluminescent device as claimed in claim 1 or 2 wherein the second charge carrier injecting layer (2) is calcium.

4. An electroluminescent device according to any of claims 1 to 3 wherein the second, barrier layer is selected from the group comprising PPV and a copolymer prepared from a precursor copolymer to PPV and poly(2,5-dimethoxy-p-phenylene-vinylene), PDMeOPV.

5. An electroluminescent device according to any of claims 1 to 3 wherein the first layer is a poly(2,5-dialkoxyphenylenevinylene) selected from the group comprising MEHPPV; poly(2-methoxy-5-(2-methylpentyloxy)-1, 4-phenylenevinylene); poly(2-methoxy-5-pentyloxy-1,4-phenylene-vinylene); and poly(2-methoxy-5-dodecyloxy-1,4-phenylene-vinylene).

6. An electroluminescent device according to any of claims 1 to 3 which comprises a third layer (32;43) between the first layer of semiconductive conjugated polymer and the second, barrier layer, the third layer being a light emissive semiconductive conjugated polymer.

7. An electroluninescent device according to claim 6 wherein the third layer is PPV processed from a tetrahydrothiophenium (THT)-leaving group precursor polymer.

8. An electroluminescent device according to claim 7 wherein there is a fourth layer (41) of an insoluble conjugated polymer converted from a precursor adjacent the first charge carrier injecting layer.

9. A method of making an electroluminescent device comprising the following steps:

providing a first charge carrier injecting layer (1) for injecting positive charge carriers;
depositing at least one layer (31;42) of a soluble semiconductive conjugated polymer which has a bandgap selected so that when excited it emits radiation;
depositing a barrier layer (33;44) onto the, or the last one of the, soluble polymer layers, said barrier layer comprising an insoluble and intractable semiconductive conjugated polymer; and
depositing onto said barrier layer a second charge carrier injecting layer (2) for injecting negative charge carriers.

10. A method of making an electroluminescent device comprising the following steps:

providing a first charge carrier injecting layer (1) for injecting positive charge carriers;
depositing onto said charge carrier injecting layer a first layer (31;41) of a soluble polymer in a solution of a first solvent;
depositing a second layer (33;44) in the form of a precursor in a solution of a second solvent;
heat treating the device so that the precursor is converted to its polymer which is insoluble; and
depositing a second charge carrier injecting layer for injecting negative charge carriers, wherein said soluble polymer, said precursor and said first and second solvents are selected so that conversion of the precursor can be carried out without damaging the soluble polymer.

11. A method of making an electroluminescent device according to claim 10 wherein there is the further step of putting down a third layer of a precursor after the second layer has dried, the heat treatment step then being carried out to convert the precursors of the second and third layers to their conjugated polymers.

12. A method according to claim 10 or 11 wherein the step of laying down the polymer and the or each precursor is done by spin coating.

13. A method according to any of claims 9 to 12 wherein the layer of a soluble polymer is MEHPPV in a solution of a first solvent selected from the group comprising: chloroform; halogenated hydrocarbon such as dichloromethane; ethers such as tetrahydrofuran; ketones such as cyclohexanone.

14. A method according to any of claim 10 to 13 wherein the second layer in the form of a precursor is PPV in a solution selected from the group comprising of methanol and water.

15. An electroluminescent device made according to the method of any one of claims 9 to 14.

Patentansprüche

1. Elektrolumineszenzvorrichtung, umfassend:

   eine erste Ladungsträgerinjektionsschicht (1), die positive Ladungsträger injizieren kann;

   eine erste Schicht (31; 42) aus einem halbleitenden konjugierten Polymer, das ein lösliches konjugiertes Polymer ist und das einen so ausgewählten Bandabstand aufweist, daß bei Anregung eine Strahlung mit einer vorher festgelegten Wellenlänge emittiert wird;

   eine zweite Ladungsträgerinjektionsschicht (2), die negative Ladungsträger injizieren kann;

   Mittel, daß ein elektrisches Feld an den Schichten aufgebaut werden kann;

   dadurch gekennzeichnet, daß die Vorrichtung zwischen der zweiten Ladungsträgerinjektionsschicht und der ersten Schicht angeordnet eine zweite, Sperrschicht (33; 44; 53) aus einem unlöslichen, halbleitenden konjugierten Polymer umfaßt.

2. Elektrolumineszenzvorrichtung nach Anspruch 1, worin die erste Ladungsträgerinjektionsschicht (1) Indiumzinnoxid (ITO) ist.

3. Elektrolumineszenzvorrichtung nach Anspruch 1 oder 2, worin die zweite Ladungsträgerinjektionsschicht (2) Calcium ist.

4. Elektrolumineszenzvorrichtung nach einem der Ansprüche 1 bis 3, worin die zweite, Sperrschicht aus der Gruppe ausgewählt wird, die PPV und ein Copolymer umfaßt, das aus einem Vorstufen-Copolymer für PPV und Poly (2,5-dimethoxy-p-phenylenvinylen), PDMeOPV, hergestellt worden ist.

5. Elektrolumineszenzvorrichtung nach einem der Ansprüche 1 bis 3, worin die erste Schicht ein Poly(2,5-dialkoxyphenylenvinylen) ist, das aus der Gruppe ausgewählt wird, die MEHPPV; Poly(2-methoxy-5-(2-methylpentyloxy)-1,4-phenylenvinylen); Poly(2-methoxy-5-pentyloxy-1,4-phenylenvinylen); und Poly(2-methoxy-5-dodecyloxy-1,4-phenylenvinylen) umfaßt.

6. Elektrolumineszenzvorrichtung nach einem der Ansprüche 1 bis 3, die eine dritte Schicht (32; 43) zwischen der ersten Schicht aus einem halbleitenden konjugierten Polymer und der zweiten, Sperrschicht, umfaßt, wobei die dritte Schicht ein lichtemittierendes, halbleitendes konjugiertes Polymer ist.

7. Elektrolumineszenzvorrichtung nach Anspruch 6, worin die dritte Schicht PPV ist, das aus einem Tetrahydrothiophenium (THT)-leaving group Vorstufen-Polymer hergestellt wird.

8. Elektrolumineszenzvorrichtung nach Anspruch 7, worin neben der ersten Ladungsträgerinjektionsschicht eine vierte Schicht (41) aus einem unlöslichen konjugierten Polymer vorliegt, das aus einer Vorstufe umgewandelt worden ist.

9. Verfahren zur Herstellung einer Elektrolumineszenzvorrichtung, das die folgenden Schritte umfaßt:

   Bereitstellen einer ersten Ladungsträgerinjektionsschicht (1) zum Injizieren von positiven Ladungsträgern;

   Abscheiden von mindestens einer Schicht (31; 42) aus einem löslichen, halbleitenden konjugierten Polymer, das einen so ausgewählten Bandabstand aufweist, daß es bei Anregung Strahlung emittiert;

   Abscheiden einer Sperrschicht (33; 44) auf der oder der letzten von den löslichen Polymerschichten, wobei die Sperrschicht ein unlösliches und schwer zu bearbeitendes, halbleitendes konjugiertes Polymer umfaßt; und

Abscheiden einer zweiten Ladungsträgerinjektionsschicht (2) zur Injektion von negativen Ladungsträgern auf der Sperrschicht.

10. Verfahren zur Herstellung einer Elektrolumineszenzvorrichtung, das die folgenden Schritte umfaßt:

Bereitstellen einer ersten Ladungsträgerinjektionsschicht (1) zur Injektion von positiven Ladungsträgern;

Abscheiden einer ersten Schicht (31; 41) aus einem löslichen Polymer in einer Lösung aus einem ersten Lösungsmittel auf der Ladungsträgerinjektionsschicht;

Abscheiden einer zweiten Schicht (33; 44) in Form einer Vorstufe in einer Lösung eines zweiten Lösungsmittels;

Hitzebehandlung der Vorrichtung, so daß die Vorstufe in ihr Polymer umgewandelt wird, das unlöslich ist; und

Abscheiden einer zweiten Ladungsträgerinjektionsschicht zur Injektion von negativen Ladungsträgern, wobei das lösliche Polymer, die Vorstufe und das erste und das zweite Lösungsmittel so ausgewählt werden, daß die Umwandlung der Vorstufe ohne Schädigung des löslichen Polymers durchgeführt werden kann.

11. Verfahren zur Herstellung einer Elektrolumineszenzvorrichtung nach Anspruch 10, das den weiteren Schritt umfaßt, eine dritte Schicht aus einer Vorstufe aufzubringen, nachdem die zweite Schicht getrocknet ist, wobei der Hitzebehandlungsschritt dann ausgeführt wird, um die Vorstufen der zweiten und dritten Schicht in ihre konjugierten Polymere umzuwandeln.

12. Verfahren nach Anspruch 10 oder 11, worin der Schritt des Aufbringens des Polymers und der oder einer jeden Vorstufe durch Spinnbeschichtung durchgeführt wird.

13. Verfahren nach einem der Ansprüche 9 bis 12, worin die Schicht aus einem löslichen Polymer MEHPPV in einer Lösung eines ersten Lösungsmittels ist, das aus der Gruppe ausgewählt wird, die umfaßt: Chloroform, halogenierte Kohlenwasserstoffe, wie Dichlormethan; Ether, wie Tetrahydrofuran; Ketone, wie Cyclohexanon.

14. Verfahren nach einem der Ansprüche 10 bis 13, worin die zweite Schicht in Form einer Vorstufe PPV in einer Lösung ist, die aus der Gruppe ausgewählt wird, die Methanol und Wasser umfaßt.

15. Elektrolumineszenzvorrichtung, die gemäß dem Verfahren nach einem der Ansprüche 9 bis 14 hergestellt worden ist.

Revendications

1. Dispositif électroluminescent comprenant :

une première couche (1) d'injection de porteurs de charge capable d'injecter des porteurs de charge positive ;
une première couche (31;42) d'un polymère conjugué semi-conducteur qui est un polymère conjugué soluble et qui a une largeur de bande interdite choisie telle que, quand elle est excitée, un rayonnement à une longueur d'onde prédéterminée est émis ;
une deuxième couche (2) d'injection de porteurs de charge capable d'injecter des porteurs de charge négative ;
des moyens pour activer un champ électrique qui sera appliqué auxdites couches ;

caractérisé en ce que le dispositif comprend, intercalée entre la deuxième couche d'injection de porteurs de charge et la première couche, une deuxième couche d'arrêt (33;44;53) fournie par un polymère conjugué semi-conducteur insoluble.

2. Dispositif électroluminescent selon la revendication 1, dans lequel la première couche (1) d'injection de porteurs de charge est un oxyde d'étain dopé à l'indium (ITO).

3. Dispositif électroluminescent selon la revendication 1 ou 2, dans lequel la deuxième couche d'injection de porteurs de charge (2) est du calcium.

4. Dispositif électroluminescent selon l'une quelconque des revendications 1 à 3, dans lequel la deuxième couche d'arrêt est choisie dans un groupe comprenant le PPV et un copolymère préparé à partir d'un copolymère précurseur de PPV et du poly(2,5-diméthoxy-p-phénylène-vinylène), PDMeOPV.

5. Dispositif électroluminescent selon l'une quelconque des revendications 1 à 3, dans lequel la première couche est un poly(2,5-dialkoxyphénylènevinylène) choisi dans le groupe comprenant MEHPPV ; un poly(2-méthoxy-5-(2-méthylpentyl-oxy)-1,4-phénylènevinylène) ; un poly(2-méthoxy-5-pentyl-oxy-1,4-phénylène-vinylène) ; et un poly (2-méthoxy-5-dodécyloxy-1,4-phénylène-vinylène).

6. Dispositif électroluminescent selon l'une quelconque des revendications 1 à 3 qui comprend une troisième couche (32;43) intercalée entre la première couche de polymère conjugué semi-conducteur et la deuxième couche d'arrêt, cette troisième couche étant un polymère conjugué semi-conducteur photoémetteur.

7. Dispositif électroluminescent selon la revendication 6, dans lequel la troisième couche est un PPV élaboré à partir d'un polymère précurseur à groupe partant tétrahydro-thiophénium (THT).

8. Dispositif électroluminescent selon la revendication 7, dans lequel il existe une quatrième couche (41) d'un polymère conjugué insoluble formé par conversion d'un précurseur, adjacente à la première couche d'injection de porteurs de charge.

9. Procédé de fabrication d'un dispositif électroluminescent comprenant les étapes suivantes :

fourniture d'une première couche d'injection de porteurs de charge (1) pour injecter des porteurs de charge positive ;
dépôt d'au moins une couche (31;42) d'un polymère conjugué semi-conducteur soluble qui a une largeur de bande interdite choisie telle que, quand elle est excitée, elle émet un rayonnement ;
dépôt d'une couche d'arrêt (33;44) sur les, ou la dernière des, couches de polymères solubles, ladite couche d'arrêt comprenant un polymère conjugué semi-conducteur insoluble et incoercible ; et
dépôt sur ladite couche d'arrêt d'une deuxième couche d'injection de porteurs de charge (2) pour injecter des porteurs de charge négative.

10. Procédé de fabrication d'un dispositif électroluminescent comprenant les étapes suivantes :

fourniture d'une première couche d'injection de porteurs de charge (1) pour injecter des porteurs de charge positive;
dépôt sur ladite couche d'injection de porteurs de charge d'une première couche (31;41) d'un polymère soluble dans une solution d'un premier solvant ;
dépôt d'une deuxième couche (33;44) sous forme d'un précurseur dans une solution d'un deuxième solvant ;
chauffage du dispositif pour que le précurseur soit converti en son polymère qui est insoluble ; et
dépôt d'une deuxième couche d'injection de porteurs de charge pour injecter des porteurs de charge négative,
dans lequel ledit polymère soluble, ledit précurseur et lesdits premier et deuxième solvants sont choisis pour que la conversion du précurseur puisse être effectuée sans endommager le polymère soluble.

11. Procédé de fabrication d'un dispositif électroluminescent selon la revendication 10, dans lequel il existe l'étape supplémentaire de dépôt d'une troisième couche d'un précurseur après que la deuxième couche a séché, l'étape de chauffage étant ensuite effectuée pour convertir les précurseurs des deuxième et troisième couches en leurs polymères conjugués.

12. Procédé selon la revendication 10 ou 11, dans lequel l'étape de dépôt du polymère et du ou de chaque précurseur est effectuée par enduction centrifuge.

13. Procédé selon l'une quelconque des revendications 9 à 12, dans lequel la couche d'un polymère soluble est un MEHPPV dans une solution d'un premier solvant choisi dans le groupe comprenant : le chloroforme, un hydrocarbure halogéné tel que le dichlorométhane ; les éthers tels que le tétrahydrofuranne ; les cétones telles que le cyclohexanone.

14. Procédé selon l'une quelconque des revendications 10 à 13, dans lequel la deuxième couche sous forme d'un précurseur est un PPV dans une solution choisie dans le groupe comprenant le méthanol et l'eau.

15. Dispositif électroluminescent fabriqué selon le procédé de l'une quelconque des revendications 9 à 14.

FIG. 1a

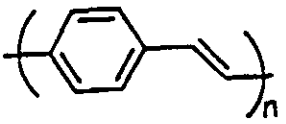


FIG. 1b

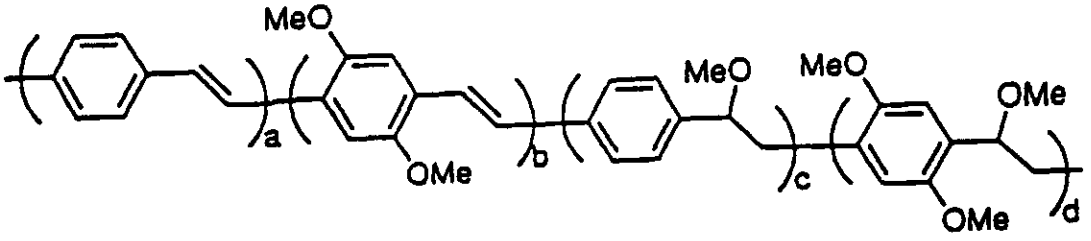


FIG. 1c

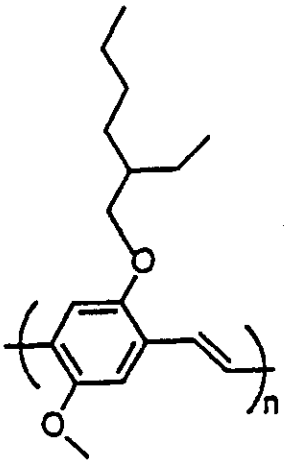


FIG. 2a

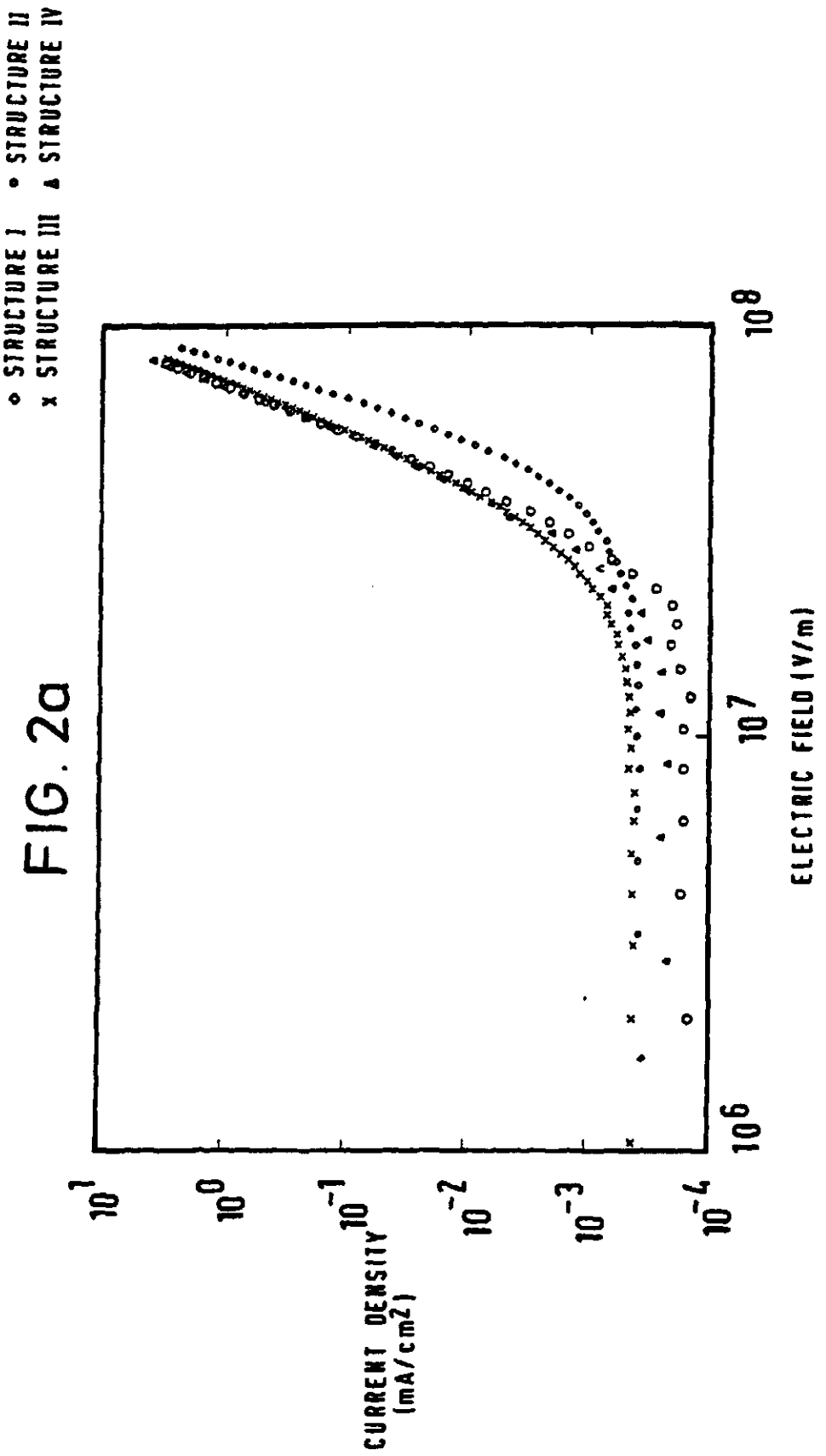
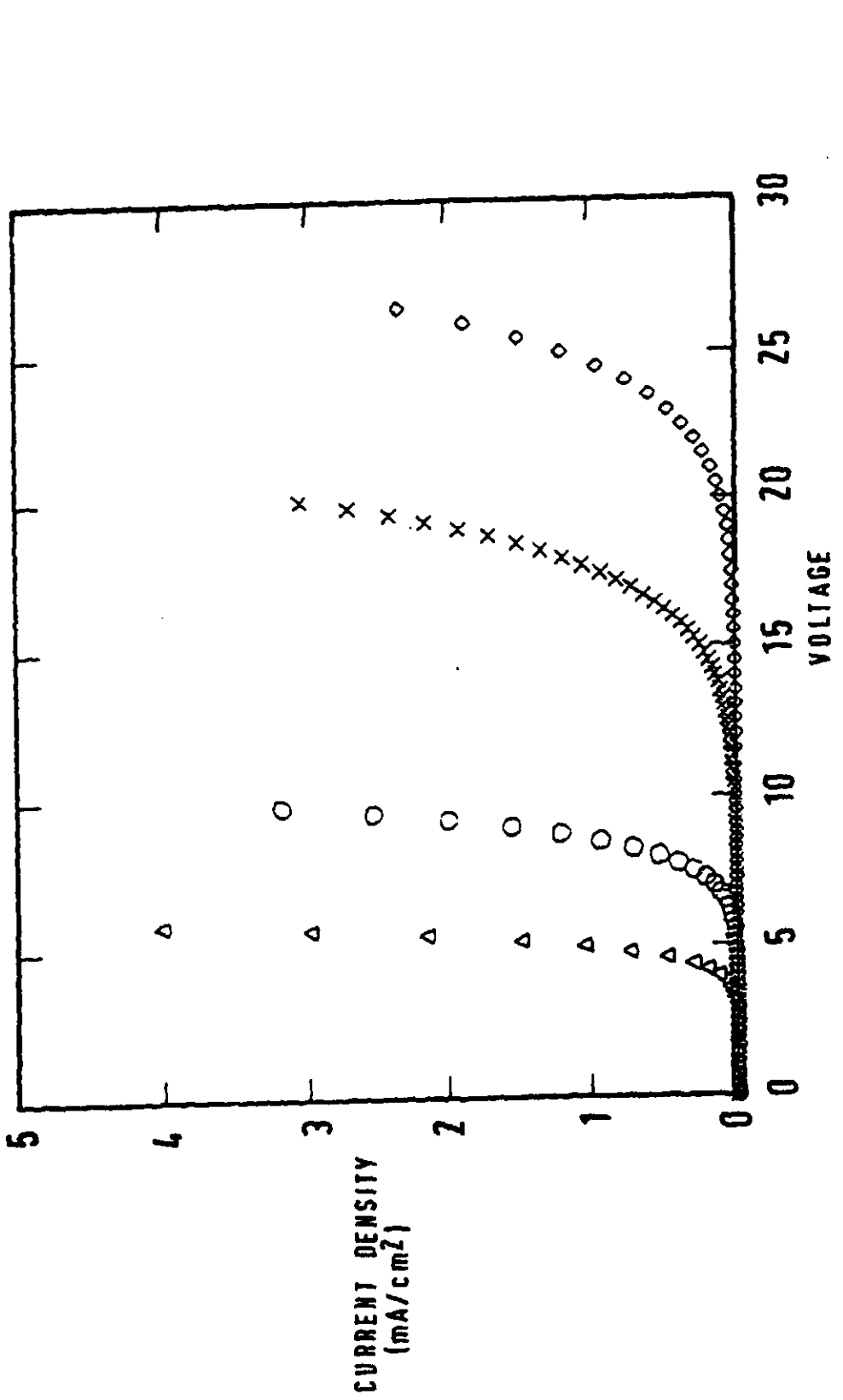

◇ STRUCTURE I
• STRUCTURE II
x STRUCTURE III
▲ STRUCTURE IV
CURRENT DENSITY (mA/cm²)
ELECTRIC FIELD (V/m)
10¹
10⁰
10⁻¹
10⁻²
10⁻³
10⁻⁴
10⁶
10⁷
10⁸

FIG. 2b


◇ STRUCTURE I
• STRUCTURE II
x STRUCTURE III
▲ STRUCTURE IV
CURRENT DENSITY (mA/cm²)
VOLTAGE
0
1
2
3
4
5
0
5
10
15
20
25
30

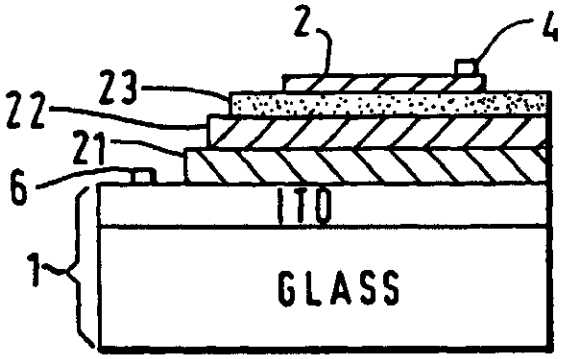


FIG. 3a

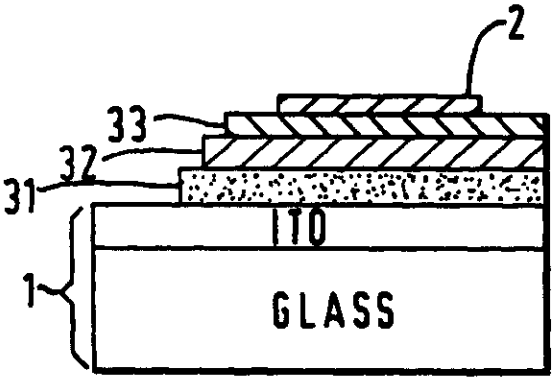


FIG. 3b

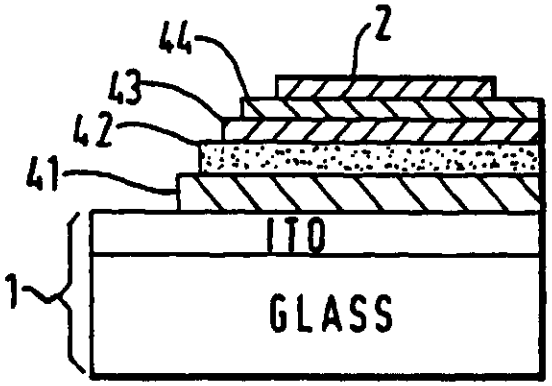


FIG. 3c

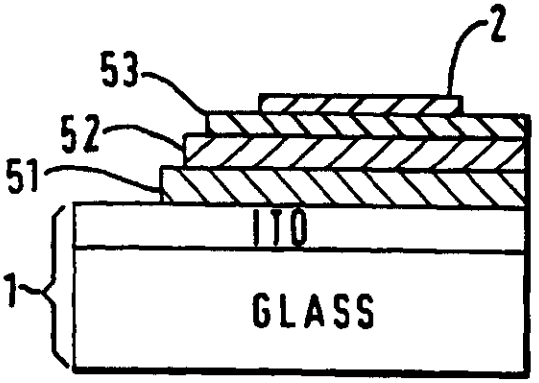
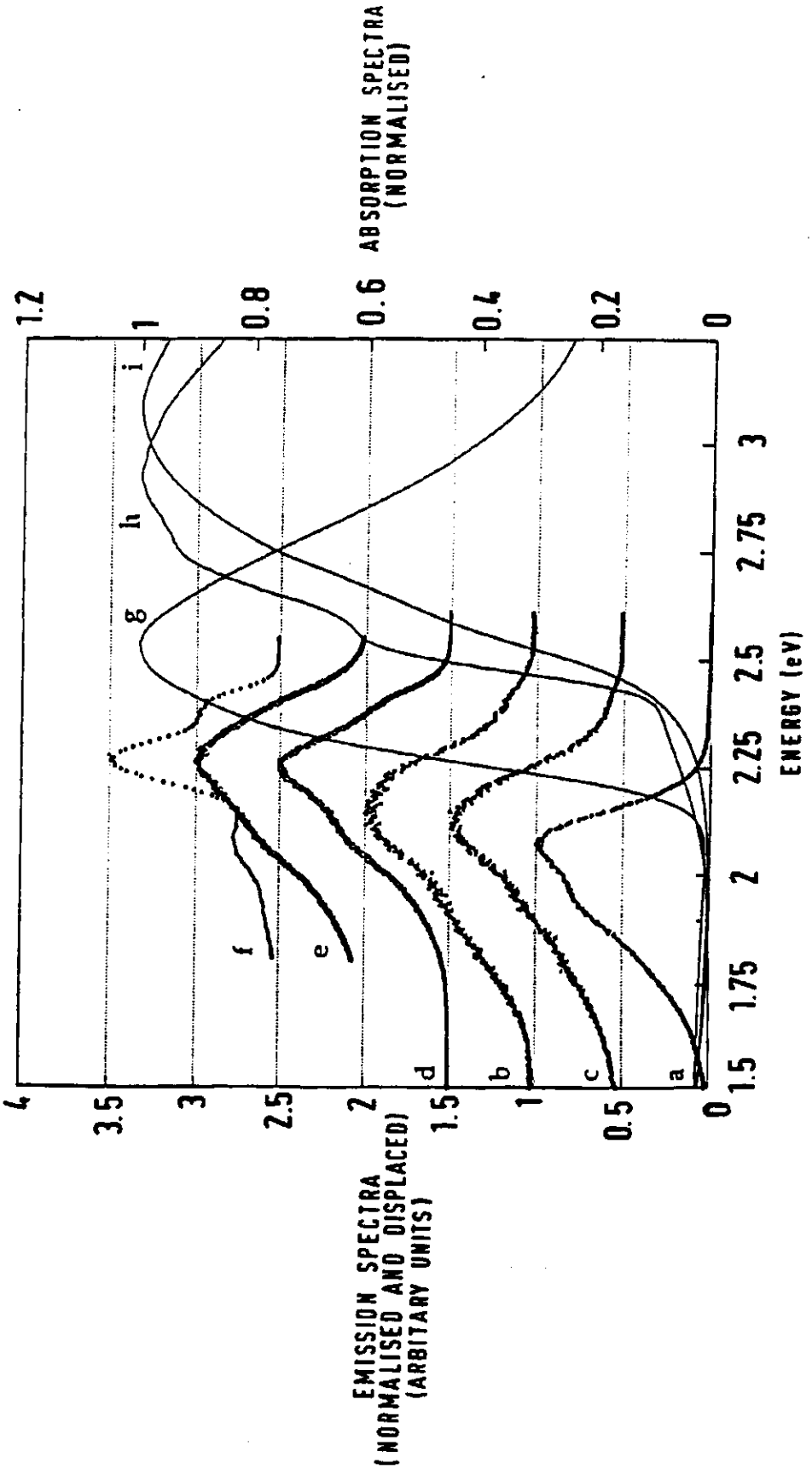


FIG. 3d

FIG. 4


ABSORPTION SPECTRA (NORMALISED)
1.2
1
0.8
0.6
0.4
0.2
0
i
h
g
f
e
d
b
c
a
4
3.5
3
2.5
2
1.5
1
0.5
0
1.5
1.75
2
2.25
2.5
2.75
3
ENERGY (eV)
EMISSION SPECTRA (NORMALISED AND DISPLACED) (ARBITARY UNITS)

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PCT EUROPEAN PHASE
PCT Application PCT/GB93/01573 Publication No WO94/03030 on 03.02.1994

Designated States DE FR GB

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**** END OF REGISTER ENTRY ****

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