

High efficiency polymer LEDs: triplets and novel devices

Eric A. Meulenkamp^{a1}, Rajan van Aar^b, J.J.A.M. Bastiaansen^c, A.J.M. van den Biggelaar^a, H. Börner^d, Klemens Brunner^a, Michael Büchel^a, Addy van Dijken^a, N.M.M. Kikken^c, Mary Kilitziraki^b, Margreet M. de Kok^a, B.M.W. Langeveld^c, Marcel P.H. Ligter^b, Simone I.E. Vulto^b, Peter van de Weijer^a, Suzanne H.P.M. de Winter^a

^a Royal Philips Electronics, Philips Research Laboratories Eindhoven, Prof. Holstlaan 4 (WAG11), 5656 AA Eindhoven, The Netherlands

^b Royal Philips Electronics, BU PolyLED, Prof. Holstlaan 4 (WZ-98), 5656 AA Eindhoven, The Netherlands

^c TNO Industrial Technology, De Rondon 1, 5600 HE Eindhoven, The Netherlands

^d Royal Philips Electronics, Philips Forschungslaboratorien Aachen, Weisshausstrasse 2, 52066 Aachen, Germany

Keywords: polymer LED, efficiency, triplet, OLED, photoluminescence, electroluminescence, anode

ABSTRACT

We present results and a discussion of highly efficient polymer Light-Emitting Diodes (polymer LEDs, PLEDs). The external quantum efficiency in current standard devices reaches up to 2-4% only. We have explored two routes to enhance this value. In the first route, PEDOT/PSS is replaced with a novel anode or hole injection layer. The efficiency with some Light Emitting Polymers (LEP) is improved significantly, resulting in an efficacy of 35 cd/A for a yellow emitting poly-(*para*-phenylene-vinylene) and 20 cd/A for a blue emitting poly-(spirobifluorene). We attribute the major improvement compared to standard devices, where about 10 and 5 cd/A are obtained, respectively, to a combination of improved exciton formation efficiency and light out-coupling efficiency, and to less quenching of the radiative decay under actual device operating conditions. In the second route, we developed a new host polymer with high triplet energy such that transition metal-based green-emitting phosphorescent dyes can be used without significant back transfer of triplet excitons to the polymer host. First results using this system showed about 25 cd/A using a soluble green Ir-based emitter. Importantly, all data are obtained in a standard two-layer device of a hole transport/injection layer and the LEP.

1. INTRODUCTION

Over the past ten years, polymer light-emitting diodes (polymer LEDs) have evolved from high power, short lifetime devices to a viable display technology that can compete with LCDs in the marketplace. Fundamental understanding and rational design of materials and devices has led to major improvements in operational lifetime and efficiency, luminance and driving voltage. In parallel, the necessary technology for large-scale manufacturing has been developed¹.

There are several benefits of polymer LEDs, or organic LEDs (OLEDs)² in general. These relate to the light generation mechanism: OLEDs are emissive displays, combining excellent viewing angle, large colour gamut, straightforward display of video content, and high contrast. OLEDs also have the capability to generate a sparkling CRT-like image. Other benefits relate to the display form factor: OLEDs are flat, thin and are light, where thin-film encapsulation offers a route to displays with the thickness of a single glass plate. Additionally, OLEDs can be made flexible while retaining the excellent display characteristics.

The performance of polymer LEDs and small-molecule OLEDs is now sufficient for first-generation products. Commercial products such as mobile phones, digital still cameras, and electric shavers incorporate OLED displays, and many companies have announced plans to introduce new products and increase manufacturing capacity in 2004. However, next generation products require even better materials and devices, with higher efficiency and longer lifetime

¹ eric.meulenkamp@philips.com; phone 31 402743346; fax 31 402743350; www.philips.com

in combination with good driving voltage and colour point. At Philips, we also pay particular attention to compatibility of performance breakthroughs with industrial-scale processing of materials and devices. In this contribution, the focus is on high external efficiency. We have explored two routes to achieve this goal: (i) development of a novel anode, and (ii) incorporation of phosphorescent dyes in a new host polymer.

2. EFFICIENCY OF PLEDs

Highly efficient devices bring many advantages. Obviously, low power is interesting in view of environmental aspects, and the promise of >70 lm/W devices, comparable to the performance of fluorescent light sources, has triggered substantial interest in OLEDs from the lighting industry. Low power is also important to successful application in hand-held battery-powered devices. A major part of power dissipation in active-matrix PLEDs (AMPLED) is related to the light generation process itself, so more efficient materials and device architectures are necessary ingredients to obtain breakthroughs in power consumption. It should be noted that low power not only means high efficacy (in cd/A), but also low driving voltage. Here the focus is on the former aspect only.

Another reason for developing highly efficient devices is the prospect of not using Low Temperature Poly-Silicon (LTPS) as the material for the back-plane electronics and pixel circuitry, but rather amorphous silicon. The latter offers an established large-scale manufacturing technology, and proven up-scaling to 46" screens. Due to the lower charge carrier mobility in a-Si a larger fraction of the available surface area is consumed by the pixel circuitry, and the transistor can deliver significantly less current. These necessitate development of PLED devices with a considerably higher efficiency.

Table I provides data obtained using the standard Philips device structure and processing (see EXPERIMENTAL section). The voltage, colour coordinate, efficacy, and external efficiency were all determined under driving conditions that may be used in a full-colour RGB AMPLED. Taking into account the aperture, the presence of a contrast-enhancing polariser, and the colour ratios needed to make D₆₅ white, we arrive at a luminance at the working point of about 1,500 cd/m² for all three colours. This also assumes a 50% duty cycle. A yellow material is included in Table I since devices using this material will be discussed in more detail below. The external quantum efficiency was calculated from the measured current density and number of emitted photons perpendicular to the device plane, assuming a Lambertian emission intensity distribution.

The external quantum efficiency (EQE) is between 2-4%. However, the efficacy values reported in Table I fulfill specifications for the first generation products. Thus, there is ample room for improvement of the device performance. A factor of 10-20× gain, depending on the colour, is not unrealistic and will demonstrate PLED devices with considerably lower power consumption than LCDs.

TABLE I. Overview of typical device performance in the standard Philips device geometry (ITO/PEDOT/LEP/BaAl) at the AMPLED working point (see text for details). Efficiency is in 100% × photon/electron. The maximum efficiency at the optimal driving condition is within 10% of the value in the working point.

Parameter	Blue	Green	Yellow	Red
CIE (x,y) coordinate	(<0.16; <0.21)	(0.39; 0.58)	(0.47;0.52)	(>0.61;<0.39)
Efficacy (cd/A)	5.0	10	12	2.5
Voltage (V)	5.0	4.5	4.5	4.0
Efficiency (ph/el) (%)	3.1	2.9	4.1	2.0

Several factors contribute to the EQE. It can be expressed as³:

$$EQE = \gamma r_{st} q C \quad (1)$$

where γ is the proportion of electrons flowing in the external circuit that produces excitons. γ includes the electron-hole balance and the efficiency of the electron-hole reaction to form an exciton. r_{st} is the fraction of excitons that is generated in the singlet state. Obviously, this can be generalized to the fraction of excitons created in a radiative state. q is the efficiency of radiative decay of the excitons, equaling the photoluminescence efficiency in many cases. C is the optical out-coupling efficiency or 'escape probability' which is the proportion of photons that exit the device in the viewer's,

i.e. front direction. Figure 1 presents a graphical view of the various efficiency loss mechanisms, together with a rough estimate of their importance in typical PLEDs.

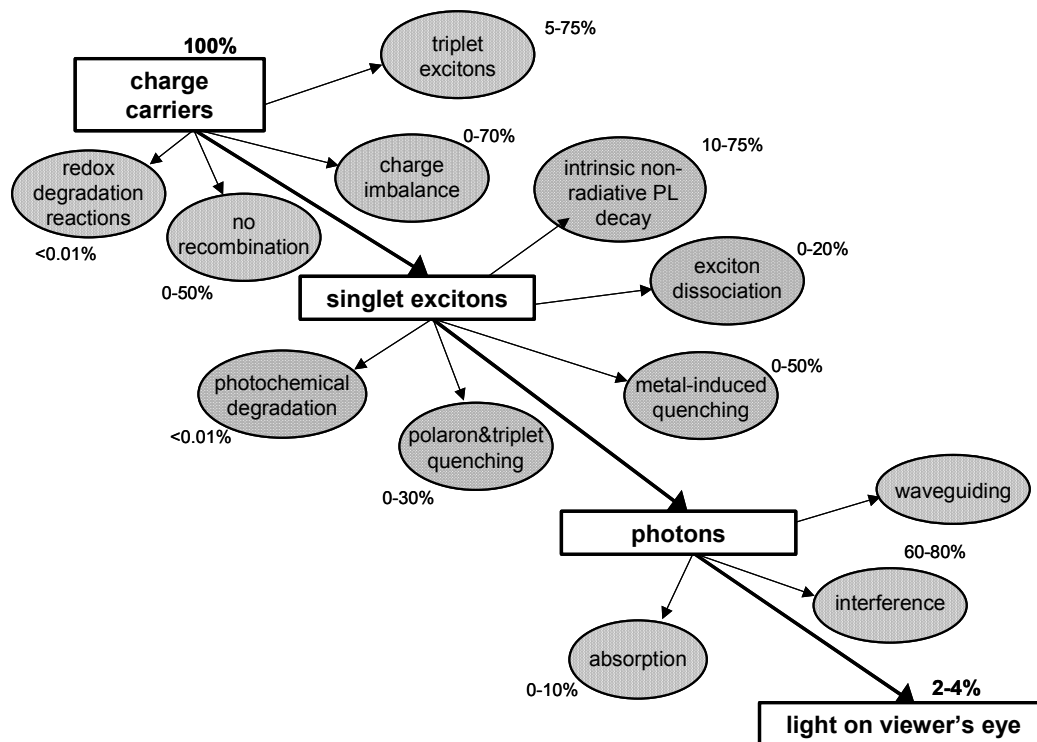


Figure 1. Graphical overview of loss mechanisms in a standard operating PLED device. The numbers refer to the percentage of charge carriers, excitons or photons following a particular pathway.

Figure 1 includes wide ranges for the estimated importance of many of the possible paths that charge carriers, excitons and photons can take. These reflect the uncertainty that exists for many of the LEPs and devices studied. Only very few studies exist which attempt to quantify all of the processes shown. We consider the following to be relatively important:

1. Fraction of charge carriers that produce excitons, in particular charge balance (“no recombination” in figure 1). In a standard PLED¹⁻³, no confinement layers for electrons or holes are present, and balanced electron and hole partial currents are achievable only by tuning of the mobility and injection of either charge carrier.
2. Fraction of excitons produced in a ‘dark’, *i.e.* triplet state (“triplet excitons” in figure 1). Quantum mechanics predict a 1:3 singlet:triplet statistical ratio³. Although the actual ratio is under debate, low formation probability of singlets is still thought to be a major issue, especially since many LEPs contain similar emitting dyes to small molecule OLEDs.
3. Non-radiative exciton decay (“intrinsic PL decay”, “exciton dissociation”, “quenching” in figure 1). LEPs are usually optimized to have high photoluminescence quantum efficiency (PLQE). However, in a working device additional quenching mechanism can operate, such as metal-induced quenching if the exciton is close to the metal cathode⁴, exciton dissociation⁵ and polaron- or triplet-induced quenching⁶ if the device is driven at high luminance.
4. Optical effects (“interference”, “waveguiding” and “absorption” in figure 1). Apart from self-absorption and absorption by PEDOT and ITO, destructive interference and waveguiding make that a significant fraction of the photons produced cannot escape to the viewer⁷.

The presence of these four main loss mechanisms can easily account for the low EQE. For example, if we suppose that each contributes 60% loss, an EQE of $(0.4)^4$ or 2.56% is expected. Obviously, some materials have lower loss in particular steps than others. In the following, we will discuss devices and LEPs that show considerably higher EQE than mentioned in Table I, and discuss the origin thereof in view of these four loss mechanisms.

3. EXPERIMENTAL

The PLEDs studied have a multi-layer device structure, as shown in Figure 2. The first layer is a structured electrode of indium tin oxide (ITO), which is cleaned by UV/ozone treatment. On the ITO layer a 100 or 200 nm layer of poly-(3,4-ethylenedioxythiophene): poly-(styrene sulphonic acid) (PEDOT:PSS)⁸, a hole-conducting layer which also serves as hole injection layer, is spin-coated from aqueous suspension. The PEDOT layer is annealed for 6 min in air at 200 °C to remove water. An 80 nm LEP layer is spin-coated from toluene on the hole-conducting layer. The light-emitting polymers used for polyLED devices are typically poly-(para-phenylenevinylene) (PPV)⁹, poly-fluorene¹⁰ and poly-spirobifluorene¹¹. Both the hole conducting layer and the light-emitting polymer (LEP) layer were deposited in air. The cathode, a low work-function metal (barium), is evaporated on the LEP, and capped with aluminium. The entire device is protected from water and oxygen using a metal lid with getter. Here we use as LEPs a yellow PPV^{9,12} and a blue and red poly-spirobifluorene¹¹, all from Covion Organic Semiconductors (Germany), for which the structures are given in Figure 3. Additionally, some new triplet host materials are discussed in section 6.

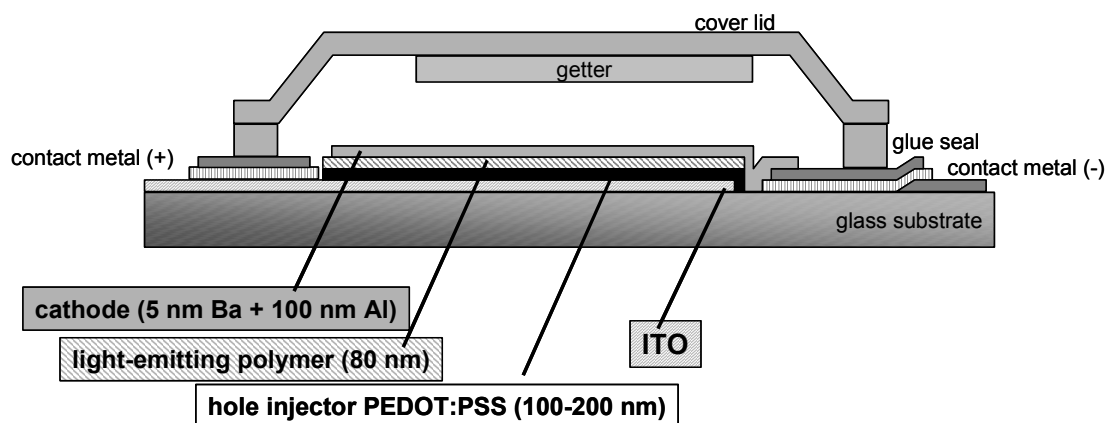


Figure 2. Schematic cross-section of PLED device build-up.

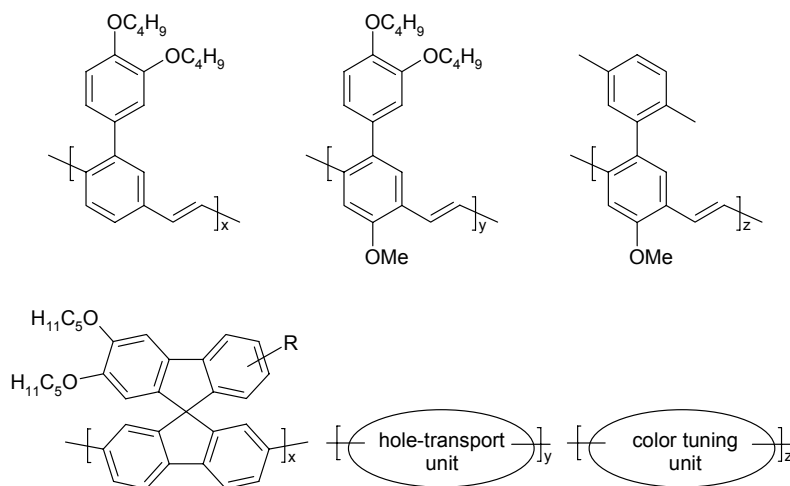


Figure 3. Chemical structures of the yellow-emitting PPV (top) and the blue and red poly-spirobifluorenes (bottom) studied. For examples of the hole-transport and colour-tuning units in the latter, please see ref. 11.

4. PL QUENCHING UNDER OPERATING CONDITIONS

One of the possible loss mechanisms in a PLED is quenching of the photoluminescence (PL) by non-radiative processes. These are already operative for a virgin film, since the PLQE is typically between 25 and 90%. This can be caused by defects that act as quenchers and by multi-phonon emission, where there is decay of the exciton by heat generation¹³. However, in a PLED additional processes can be at work. To study this, the PL of standard devices was studied as a function of potential under reverse and forward bias.

Under reverse bias, continuous wave (*cw*) excitation was used in combination with an applied *dc* voltage, and the PL intensity was monitored. At low forward bias, pulsed light excitation was applied in combination with a *dc* voltage (Figure 4a). By using gated detection and under the condition that the PL intensity is much larger than the simultaneous electroluminescence (EL), the measured signal directly gives the PL intensity as a function of voltage. At high forward bias a different measurement technique was used (Figure 4b), where a *cw* Ar or Kr laser excitation source was combined with pulsed electrical excitation (<1 ms pulse length, < 2% duty cycle). This set-up was used to obtain a measurable PL signal that can be selected from the (large) EL background, while avoiding excessive heat generation due to driving under high bias. In the reference experiment the laser source was blocked. The EL and the sum of EL and PL were monitored on an oscilloscope.

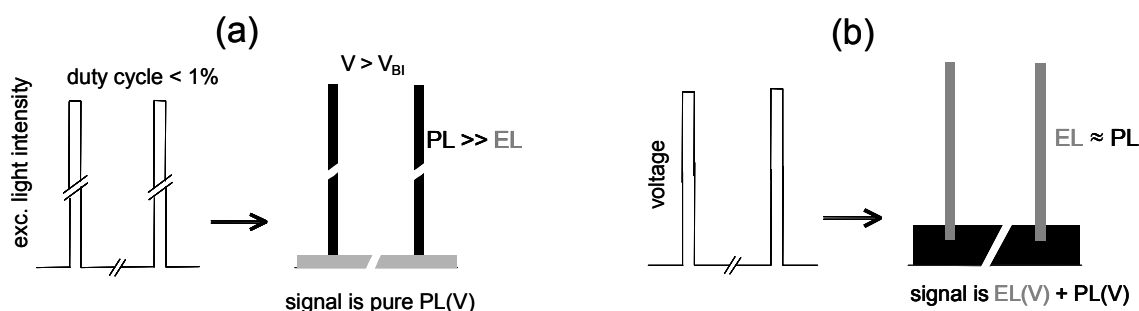


Figure 4. Measurement approaches used to discriminate PL from EL at low (left) and high (right) forward bias.

The first set of experiments was performed with the yellow PPV (Figure 5). 50% quenching was observed at about -15 V for an 80 nm LEP film. This corresponds to about 2.1×10^6 V/cm, taking into account a built-in voltage V_{BI} of 1.7 V (Figure 5b, filled circles). By comparing devices with various LEP thickness, it was established that exciton quenching was entirely determined by the electric field. Moreover, no difference between double-carrier and hole-only devices (Au cathode) was observed at a given reverse field.

Surprisingly, figure 5a shows that PL quenching was already observed at V_{BI} , the degree of quenching being smaller for thicker films. This was explained by an interfacial doping interaction between PPV and PEDOT:PSS¹⁴. In the absence of PEDOT:PSS, less PL quenching was found. Hardly any quenching was observed with hydrogen plasma-treated ITO as anode; this anode has a low work function and the hole injection rate is small. Again, the same results were found with a double-carrier and hole-only device.

The significance of these results is in the consequences for the device efficiency. For example, at about 5 V the PL efficiency is $> 25\%$ lowered compared to the maximum at about -4 V. Moreover, it is not clear whether any interaction between PEDOT and LEP has taken place that cannot be undone at some voltage. In other words, the maximum PLQE of this PPV film in the actual device may be lower than that of a pristine film on quartz, where we measured a value of 41%. Thus, calculations on *e.g.* the singlet/triplet (S/T) ratio have to take into account possible PL quenching, even when the S/T ratio is evaluated at low forward bias. This introduces some additional uncertainty, in particular because the location of the PL and EL emission may differ, due to in-coupling and out-coupling of light and the location of the EL emission zone.

It was found that the PL quenching at V_{BI} and at low forward bias is most prominent for PPV-based materials. The blue- and red-emitting poly-spirobifluorene did not show quenching. An example can be seen in Figure 5b (filled triangles) for a red LEP.

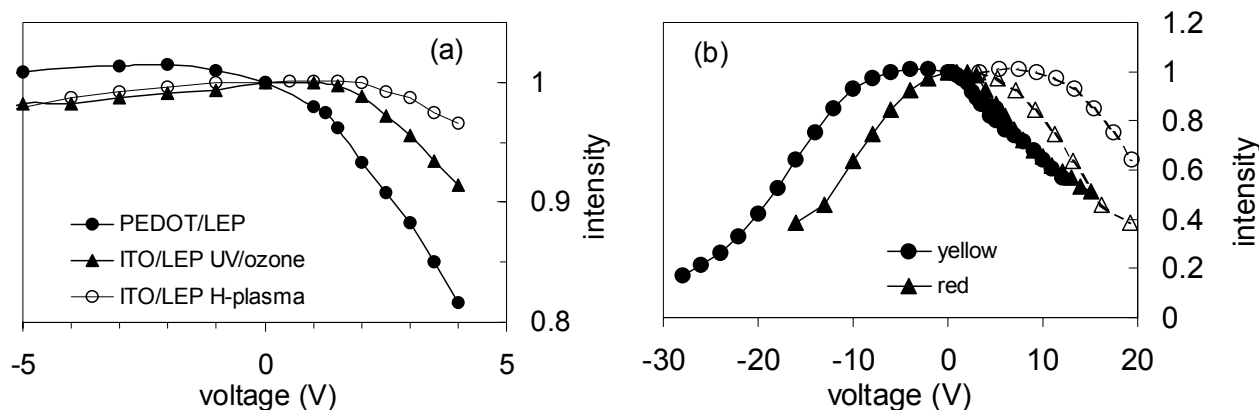


Figure 5. Quenching of PL as a function of bias for a yellow PPV ((a), and filled circles in (b)) and for a red poly-spirobifluorene ((b), filled triangles). The effect of the anode on the PPV PL quenching around V_{BI} is shown in (a). (b) shows results over a wider voltage range. The open symbols in (b) show calculated data at forward bias assuming field-induced quenching of the same magnitude as at reverse field, *i.e.* the curves with open symbols are mirror images with respect to V_{BI} of the measurements at reverse bias. The closed symbols show the actual measurements at forward bias.

Figure 5 also shows results at high forward bias. At about 14 V, close to 50% PL quenching is observed for both LEPs. It is also clear that quenching at a given forward field is considerably larger than at the same reverse field (compare open and closed symbols, see figure caption). With the PPV this is, at least partly, caused by the PEDOT:PSS/LEP interaction discussed in ref. 14. However, the data for the red LEP show that other effects also play a role. One possibility is that PL is quenched more strongly in forward bias because of the non-linear potential distribution with the space-charge limited current in the device. Thus, it may be that PL measurements sample exciton properties from a region of considerably higher field than average. In addition, quenching by interaction with triplet excitons and charge carriers (polarons) can occur.

Another interesting aspect of PL quenching is shown in figure 6: it strongly resembles EL quenching at the same voltage. This strongly suggests that the roll-off of EL efficiency at high bias is related to exciton quenching. A quantitative comparison is again complicated by possible differences in sampling position of EL and PL. This finding may also have some implications for device lifetime: it points out that at high bias a small fraction of electrons and holes reaches the opposite electrode. Several recent papers¹⁵ have pointed out that injection changes due to electrical stress may be the origin of PLED degradation. Interfacial reactions are thought to induce such changes. Electrons and holes reaching the anode and cathode, respectively, are likely candidates to initiate these interfacial reactions.

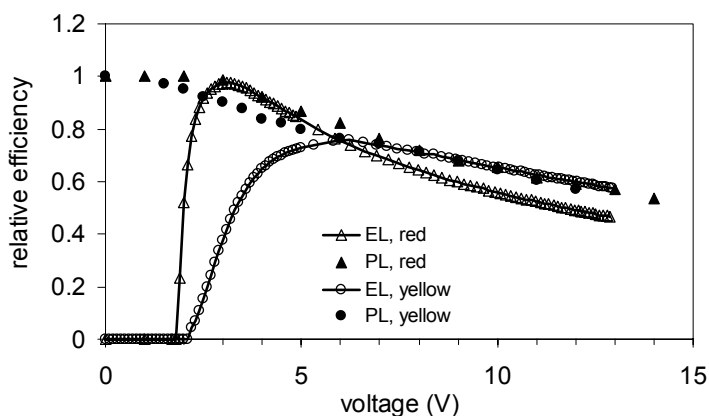


Figure 6. Comparison of EL (line and open symbols) and PL (closed symbols) as a function of voltage for a yellow PPV (circles) and a red poly-spirobifluorene (triangles).

5. POLYMER LEDs WITH A NOVEL ANODE

In the previous section data were reported for the standard PEDOT:PSS anode. Recently, we have looked at some alternative hole injection layers. Results for one of these with yellow PPV are collected in figure 7. The standard anode yields about 10 cd/A around 5 V. The efficacy decays slightly at higher voltage, as discussed in section 4. Application of the novel anode results in markedly different device characteristics. The efficacy at low voltage is only a few cd/A. However, a huge improvement in performance is seen at higher voltage, with a maximum of about 35 cd/A (7 lm/W) around 15 V, corresponding to a luminance of $>350,000$ cd/m². We believe that this is the first time such a high efficacy has been reported at such a high luminance in an OLED device.

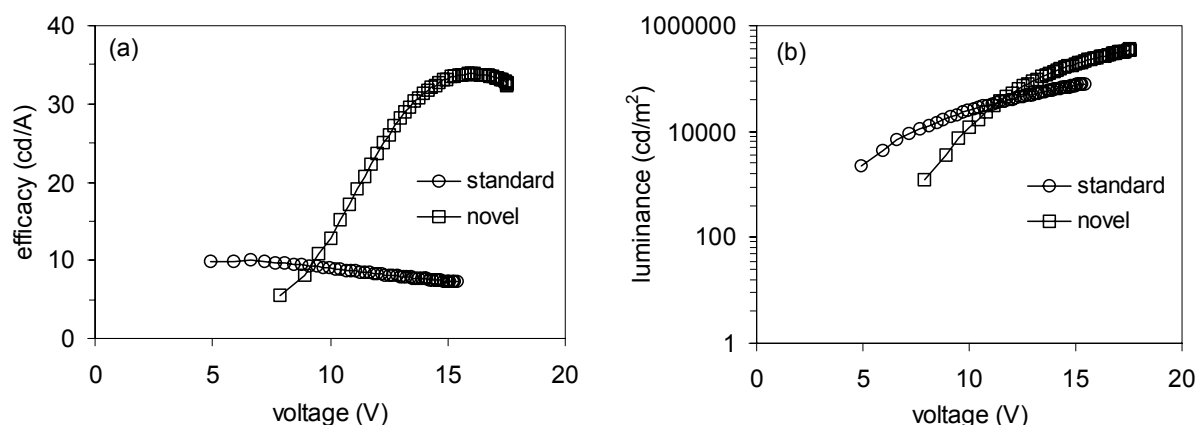


Figure 7. Voltage dependence of the efficacy (a) and luminance (b) of PLEDs based on yellow PPV using the standard anode and the novel anode.

The benefit of the novel anode was also studied with other LEPs. Figure 8 shows results for the blue poly-spirobifluorene. The standard anode gives about 5 cd/A at low voltage, with the usual roll-off at higher bias to about 3 cd/A at 14 V (1.1 A/cm² or 30,000 cd/m²). The novel anode again shows markedly improved values of about 20 cd/A at intermediate voltage, and over 150,000 cd/m² at 14 V (1.1 A/cm²). To the best of our knowledge, such high efficacy for a blue LEP (CIE coordinates 0.16;0.21) has never been reported before, with either fluorescent or phosphorescent small-molecule or polymer materials.

It is clear that both the yellow and blue LEP show a different dependence of efficacy on voltage with the novel anode, with the maximum at higher voltage than with the standard anode. To investigate this in more detail, we looked at the current-voltage (I-V) curve for the yellow PLEDs.

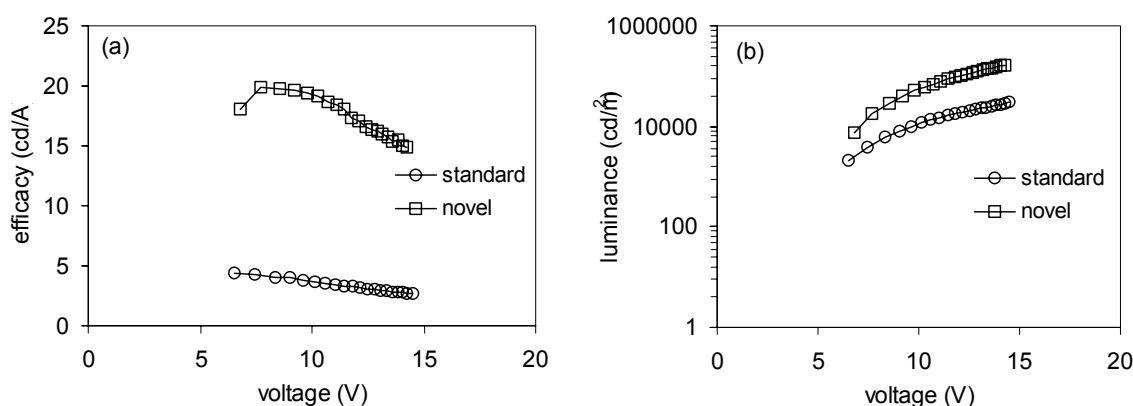


Figure 8. Voltage dependence of the efficacy (a) and luminance (b) of PLEDs based on blue poly-spirobifluorene using the standard anode and the novel anode.

Figure 9 shows (I-V) data for hole-only devices (Au cathode) and double-carrier devices (Ba/Al cathode) using the standard and the novel anode. The current density in the double-carrier PLED (figure 9a) is roughly two orders of magnitude lower at low to intermediate voltage. Since the bulk LEP properties are not affected by the choice of anode, the lowered current must be related to the presence of an injection barrier. This is confirmed by investigation of the current in hole-only devices, see figure 9b. The current density with the novel anode is several orders of magnitude lower than with the standard PEDOT:PSS anode. Actually, the measured current is mostly leakage current, *i.e.* the true device current is even lower.

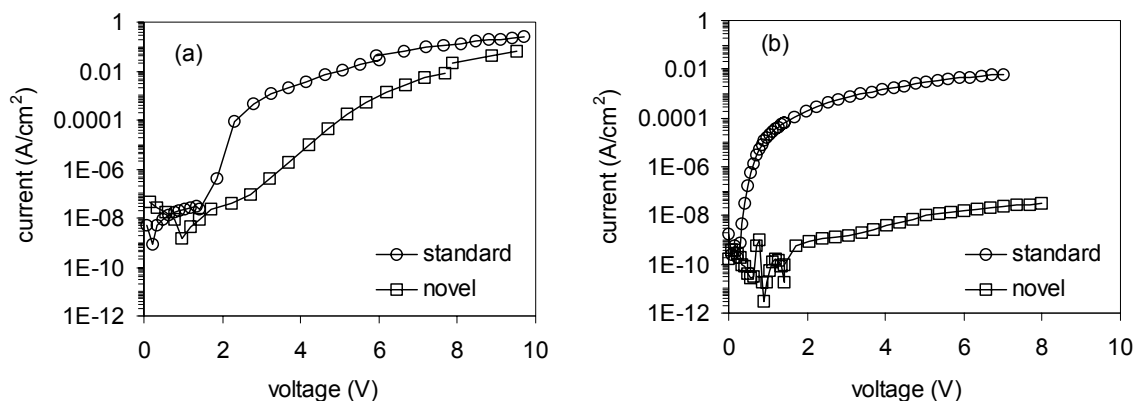


Figure 9. Current-voltage curves for yellow PPV. (a) and (b) show data for double-carrier and hole-only devices, respectively, using the standard and the novel anode.

In the literature there is evidence that holes are the dominant carriers in typical PPV-based LEPs¹⁶. This brings us to the following explanation for the high efficiency observed. A schematic picture of the device performance is shown in figure 10. With the standard anode (figure 10a), imbalance in the bulk mobility of holes and electrons can lead to an imbalance in hole and electron partial currents, assuming ohmic injection of either charge carrier. The latter was confirmed by the space-charge limited behaviour of hole-only and double-carrier devices. Use of a different cathode such as Ca did also not affect the current density. As a consequence of the high hole mobility, exciton formation and light emission occur relatively close to the cathode. It is well known that destructive interference and quenching by the metal then lead to loss of external efficiency⁷. PL quenching presents a further mechanism for loss of efficiency, as discussed in conjunction with figure 1 and 5a.

With the novel anode, three loss mechanisms are considerably reduced in importance. The imbalance in hole and electron partial currents is changed by introduction of a barrier to hole injection. Apparently, a good balance is obtained at high voltage, as seen in figure 7 and 8. As a consequence, the out-coupling of light is much more efficient, since destructive interference loss is minimal when the emission zone is about 60 nm from the cathode⁷, *i.e.* close to the anode in our 80 nm LEP device. Thirdly, the PL quenching is considerably reduced. With the novel anode it was measured that PL as a function of voltage did not show the marked intensity decrease at low voltage. Unfortunately, we were not able to measure the amount of PL quenching at high voltage, because the extremely high EL intensity precluded sufficiently accurate determination of the much lower PL intensity.

The effect of the novel anode was also studied with other LEPs. It was found that major improvements in efficiency were not present in all cases. This is probably a consequence of the particular device characteristics obtained with some LEPs. For example, use of the novel anode in combination with a material that gives an electron-dominated device with the standard anode, would be expected not to result in a highly efficient device. Such aspects are currently being investigated in more detail, as is the device lifetime.

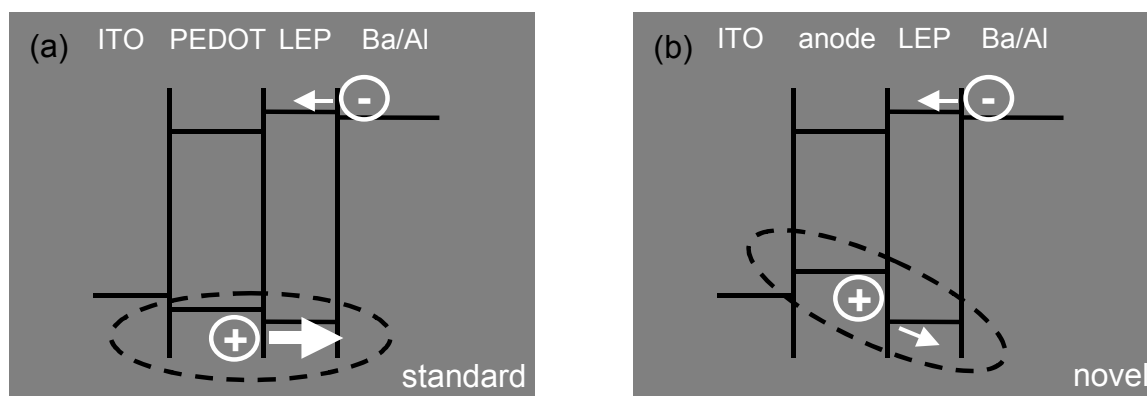


Figure 10. Schematic picture of the difference between the device characteristics using the standard anode and the novel anode.

Recently, interest in the singlet/triplet (S/T) ratio in PLEDs has increased considerably, owing to several reports that showed S/T ratios clearly exceeding the 1:3 quantum statistical prediction that was previously considered to impose a fundamental limit to internal device efficiency of 25%. Several approaches to measure the S/T ratio have been developed. These rely on a rather complex series of experiments, requiring assumptions on *e.g.* the optics of the device, or using special devices or specially prepared LEPs¹⁷. While there are also some uncertainties regarding the devices discussed above, it is possible to extract an estimate of the minimum S/T ratio ($r_{S/T}$) from the results of figure 7 and 8.

According to equation 1, calculation of $r_{S/T}$ requires determination of EQE (photon/electron), γ (the proportion of electrons flowing in the external circuit that produces excitons), q (the PLQE) and C (the optical out-coupling efficiency). The maximum EQE for the yellow and blue LEPs was 12.0 and 12.5% respectively. γ cannot be determined by a measurement. By definition, it is $\leq 100\%$, resulting in a lower limit to $r_{S/T}$. PLQE was measured for pristine films on quartz using an integrating sphere as described in the literature¹⁸. Its value was 38% for blue, and 41% for yellow. The actual value at the driving condition giving the maximum efficiency was not determined. The measured values thus present upper limits.

Therefore, $C \times r_{S/T}$ is $\geq 29\%$ and $\geq 33\%$, respectively. Exact calculation of C requires accurate determination of all optical constants, the dipole orientation, the radiative and non-radiative lifetime of an isolated dipole, layer thickness, and the location of the emission zone⁷. This requires, amongst others, use of a rather sophisticated optical model. However, an estimate can be made on the basis of existing literature. A maximum value of C of 50% seems reasonable^{4,7,17c,19}, assuming optimal location of the emission zone and pure in-plane dipoles. This results in an S/T ratio of $\geq 60\%$ for both LEPs, in good accordance with other results on the S/T ratio in similar LEPs.

It should be noted that the minimum value of about 60% indicates that the devices with the novel anode operate close to optimal with respect to charge balance, exciton formation, and location of the emission zone. Actually, the major loss mechanism appears to be in the PLQE. Thus, LEPs with higher PLQE may bring even more efficient PLED devices.

6. PHOSPHORESCENT POLYMER LEDs

In the previous sections we restricted ourselves to fluorescent polymer LEDs. It was shown that the internal efficiency can be far from optimal in a standard device, while in a device with the new anode the recombination efficiency is close to one. In the LEPs discussed in the previous section the S/T ratio considerably exceeds 25%, enabling very high EQE. However, not all light-emitting materials can be expected to show this advantageous feature. Therefore, routes towards harvesting triplet excitons are needed.

Only few organic molecules show radiation from the first triplet state at room temperature (phosphorescence). Therefore, the emission in conventional OLEDs is due to fluorescence of the excited molecules. An elegant way to use phosphorescence *and* fluorescence, *i.e.* all excited states formed in an OLED, is the introduction of phosphorescent emitters in the emissive layer²⁰. These can harvest *both* the triplet *and* the singlet excitations formed in the emissive layer and thereby use all excited states for the emission of light.

One of the main issues in PLEDs concerns the triplet energy gap of the polymer host materials in which the phosphorescent emitters are to be employed. That is, the triplet energy gap of the host has to be higher in energy than the triplet energy of the phosphorescent guest. Up to now only a very limited number of polymers has been described, such as the hole transporting UV polymer poly(9-vinylcarbazole) (PVK), which have a triplet energy sufficiently high to host phosphorescent emitters with an emission color other than red or orange²⁰. Moreover, PVK and its derivatives have several disadvantages that limit their applicability in PLEDs. Charge transport is dominated by holes²¹, and the LEPs are unstable and have a very 'deep' HOMO that makes efficient charge injection difficult.

Common to the molecular structure of the carbazole derivatives mentioned above is derivatization via the nitrogen atom in the carbazole unit. Here we introduce²² alternative carbazole derivatives based on substitution at the phenyl rings of the carbazole unit²³. One of the building blocks is 9,9'-dialkyl-[3,3']-bicarbazolyl (figure 11, **1**), which is built into the main chain of the polymer such that all sites prone to the oxidative degradation known in carbazoles, are protected. The other building block of the copolymer is either 2,5-diphenyl-[1,3,4]-oxadiazole (figure 11, **2**) or 9,9-bis[4-(3,7-dimethyloctyloxy)phenyl]fluorene (figure 11, **3**), which ensures a reasonable charge carrier balance by adding electron transport character to the copolymer.

In this class of carbazole copolymers, the delocalization of triplet excitons can be limited such that the copolymers have a triplet energy of about 2.6 eV. Data are collected in Table II. As a first order approximation one can say that the triplet energy of the carbazole compounds studied here is determined by the longest poly(*p*-phenyl) chain that can be identified in the molecular structure. This is highlighted in figure 11 by the dashed rectangle. To maintain a high triplet energy in a copolymer, the longest poly(*p*-phenyl) chain in the molecular structure should be as short as possible. This can be achieved by connecting the monomers via a *meta* coupling instead of a *para* coupling. The coupling site is indicated in figure 11 by the numbers next to the ring atoms.

The triplet energy of the polymers **1** – **3** of approximately 2.6 eV is significantly higher than that of poly-(fluorene) (2.2 eV – 2.4 eV)²⁴ and poly-(*para*-phenylenevinylene) (1.3 eV – 1.6 eV)²⁵, and lower than that of PVK (~ 3 eV). In fact, the triplet energy of the carbazole polymers **1** - **3** matches that of 4,4'-bis(9-carbazolyl)-biphenyl (CBP), which has a triplet energy of 2.56 V²⁵.

For the copolymers the values of the half-wave oxidation potential (about 0.75 V, see table II) are slightly larger than that of the homopolymer (0.55 V, see Table II) but still considerably lower than that of PVK (ca. 1.1 V). For the carbazole-oxadiazole copolymer **2** and the homopolymer **1**, the ionization potential was also determined with UPS, which yielded a value of 5.1 eV for both (the differences seen in the CV measurements are not reflected in the UPS measurements). These results can be used to compare the ionization potential of the new polymers to the work function of the charge injection contacts, *viz.* PEDOT:PSS, and Ba/Al, which have also been determined with UPS. The HOMO level of the carbazole copolymers is close to the Fermi level of PEDOT:PSS at -4.9 eV, resulting in a good hole injection contact. This is a major improvement with respect to PVK, where a hole injection barrier of about 1 eV exists at the PEDOT:PSS / PVK interface.

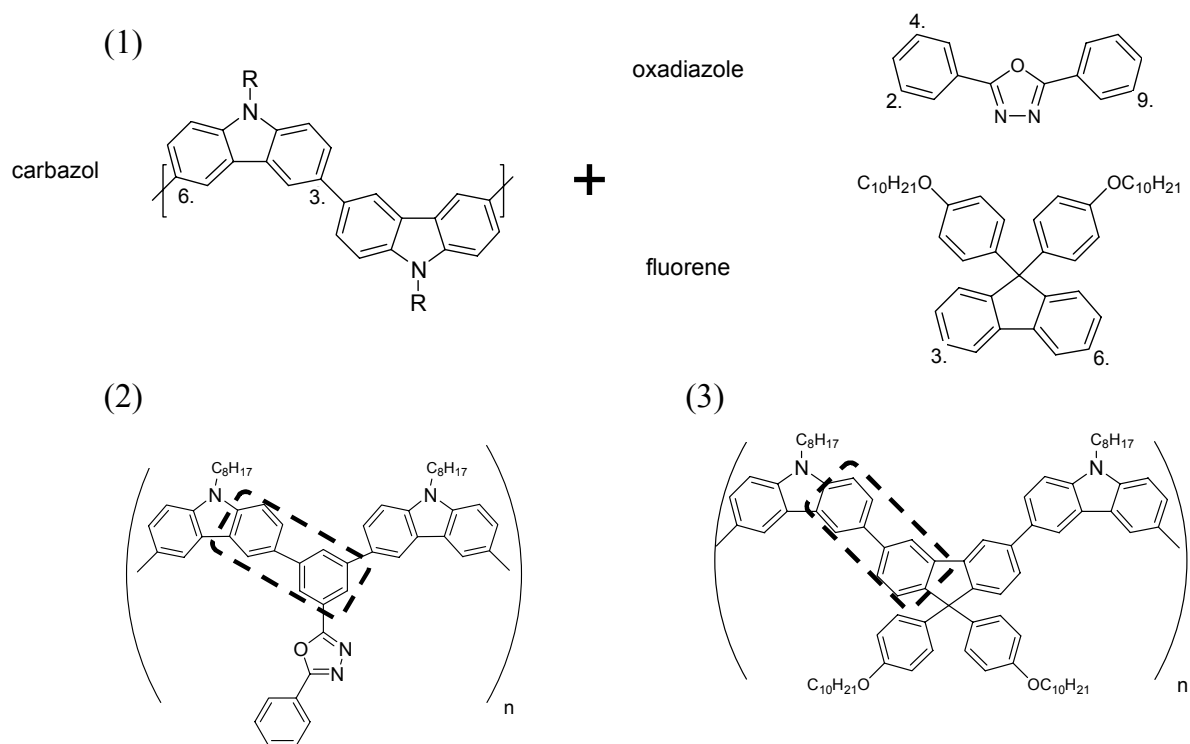


Figure 11. Chemical structures of the carbazole homopolymer (1), the carbazole-oxadiazole copolymer (2), and the carbazole-fluorene copolymer (3). Oxadiazole and fluorene units are built into the polymer chain via a meta link. The numbers indicate the preferred site of connecting the monomers to achieve copolymers with high triplet energy and the dashed squares indicate the longest *para* connected phenyl chain in the copolymers.

Table II. Half-wave oxidation potential (vs saturated Ag/AgCl), onset of absorption, and energy of the triplet emission ($S_0 \leftarrow T_1$), for the carbazole homopolymer, carbazole-oxadiazole and carbazole-fluorene copolymers.

		Abs.	$S_0 \leftarrow T_1$
	$E_{1/2}$	E_{onset}	ΔE
	[V]	[eV]	[eV]
1.	0.55	3.2	2.60
2.	0.75	3.1	2.56
3.	0.76	3.2	2.60

A standard PLED containing a layer of the carbazole-oxadiazole copolymer **2** into which the green light-emitting triplet emitter Ir-SC4 (see caption in figure 12) is molecularly dispersed with a concentration of 8 wt-% shows a high efficiency of 24 cd/A. The efficiency does not decrease at high current density and high luminance level, as shown in figure 12. The emission of the device originates exclusively from the green triplet emitter. Evaporating a hole or exciton blocking layer such as 1,3,5-tris(phenyl-2-benzimidazole)-benzene (TPBI) on the doped copolymer **2** does not improve the efficiency for devices with BaAl cathodes considerably.

These results demonstrate that a high-energy triplet emitter dispersed in a polymer host can be made to emit efficiently in a standard two-layer PLED device architecture. It is expected that further optimization of the copolymer composition will result in still higher efficiency by improving the PLQE of the emitter and the balance between the hole and electron partial currents.

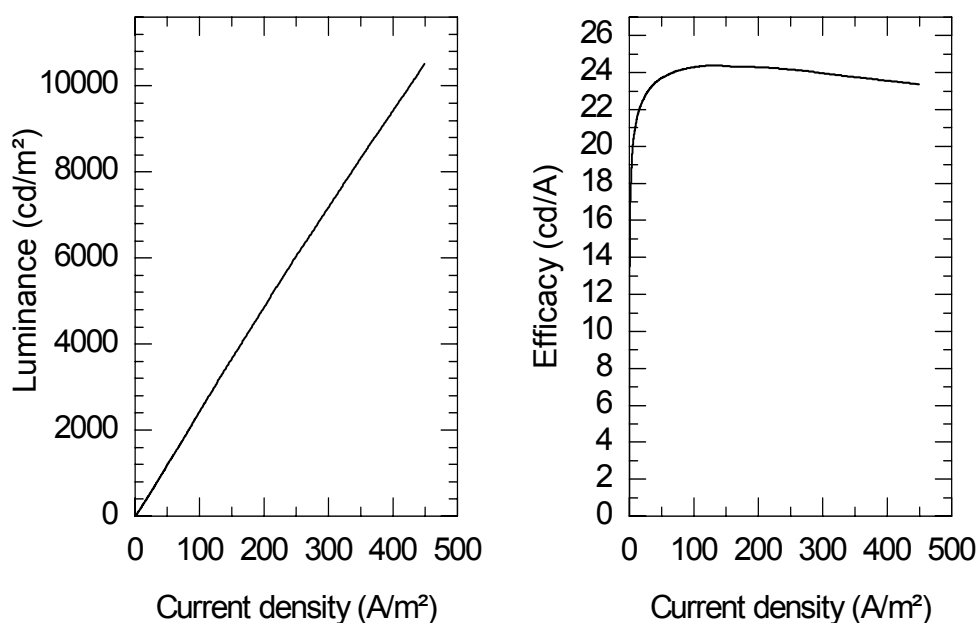


Figure 12. Efficacy and luminance as a function of current density for doped PLEDs containing a layer of the carbazole-oxadiazole copolymer **2**. The phosphorescent emitter fac-tris[2-(2-pyridinyl-kN)(5-(3,4-bis(2-methylpropyloxy)phenyl) phenyl)-kC]-iridium(III) (Ir-SC4, Covion Organic Semiconductors GmbH) is dispersed in the copolymer layer at a mass ratio of 8 %. The green emission is solely due to the phosphorescent emitter.

7. CONCLUSIONS

High efficiency in polymer LEDs is important to their future application in displays and lighting. The low external quantum efficiency (EQE) in current standard devices is related to four major contributions. Thus, there exist several pathways to enhance EQE. Two routes were explored here: (i) development of a novel anode, and (ii) incorporation of phosphorescent dyes in a new host polymer.

It was shown that for some light-emitting polymers introduction of the new anode leads to significantly higher EQE of up to about 12%, pointing out the importance of electron-hole balance, out-coupling and photoluminescence quantum yield under operating conditions. The EQE was used to estimate a minimum value of the singlet/triplet ratio of 60%.

A new strategy to design hosts suited to efficient green triplet emitters was introduced. This is based on confinement of the triplet exciton to a small section of the polymer chain, by minimizing the number of *para*-conjugated phenylene units. First results showed an efficacy of about 25 cd/A. Together, these results underline the potential increases in polymer LED performance, without compromising one of its attractive features, *viz.* the two-layer device architecture that is attractive from an industrial point of view.

ACKNOWLEDGEMENTS

We would like to thank all project members in Philips Research Eindhoven (The Netherlands), Philips Research Aachen (Germany) and Philips Mobile Display Systems in Heerlen (The Netherlands). We thank our collaborators at Covion Organic Semiconductors GmbH and H.C. Starck for discussion and for supplying materials. The triplet host work was done in collaboration with C. Rothe and A. Monkman (Durham, UK). The soluble triplet emitter was provided by Covion Organic Semiconductors GmbH. Parts of this work were supported by the European Commission under GDR1-2000-25820 (POWERPLAY) and IST-2001-37375 (STEPLED)), and by the Dutch Ministry of Economic Affairs under the BTS programme (BLUELED).

REFERENCES

- 1 see, *e.g.* E.I. Haskal, M. Büchel, P.C. Duineveld, A. Sempel and P. Van de Weijer, *MRS Bull.* **27**, 864 (2002)
- 2 C.W. Tang and S.A. Van Slyke, *Appl. Phys. Lett.* **51** (1987) p. 913, J.H. Burroughes, D.D.C. Bradley, A.R. Brown, R.N. Marks, K. MacKay, R.H. Friend, P.L. Burn and A.B. Holmes, *Nature (London)* **347** (1990) p. 539
- 3 J. Kalinowski, *J. Phys. D: Appl. Phys.* **32** (1999) p. R179; N.K. Patel, S. Cinà and J.H. burroughes, *IEEE J. Select. Topics Quantum Electronics* **8**, 346 (2002)
- 4 H. Becker, S.E. Burns and R.H. Friend, *Phys. Rev. B* **56**, 1893 (1997)
- 5 V.I. Arkhipov, H. Bässler, M. Deussen, E.O. Göbel, R. Kersting, H. Kurz, U. Lemmer and R.F. Mahrt, *Phys. Rev. B* **52**, 4932 (1997); S. Tasch, G. Kranzelbinder, G. Leising and U. Scherf, *Phys. Rev. B* **55**, 5079 (1995)
- 6 P. Dyreklev, O. Inganäs, J. Paloheimo and H. Stubb, *J. Appl. Phys.* **71**, 2816 (1992); E.J.W. List, C.-H. Kim, A.K. Naik, U. Scherf, G. Leising, W. Graupner and J. Shinar, *Phys. Rev. B* **64**, 155204 (2001)
- 7 W.L. Barnes, *Contemp. Physics*, **41**, 287 (2000); P.A. Hobson, J.A.E. Wasay, I. Sage and W.L. Barnes, *IEEE J. Select. Topics Quantum Electronics* **8**, 378 (2002);
- 8 L. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik, and J.R. Reynolds, *Adv. Mater.* **12**, 481 (2000)
- 9 H. Becker, H. Spreitzer, W. Kreuder, E. Kluge, H. Schenk, I. Parker, and Y. Cao, *Adv. Mater.* **12**, 42 (2000)
- 10 M.T. Bernius, M. Inbasekaran, J.O'Brien, and W. Wu, *Adv. Mater.* **12**, 1737 (2000)
- 11 H. Becker, A. Büsing, A. Falcou, S. Heun, A. Parham, P. Stoessel, H. Spreitzer, K. Treacher, and H. Vestweber, *Proceedings of the International Society for Optical Engineering (SPIE) (USA)*, Meeting San Diego 2001, **4464**, 49 (2002)
- 12 H.J. Bolink, M. Büchel, B. Jacobs, M.M. de Kok, M. Ligter, E.A. Meulenkaamp, S. Vulto, and P. van de Weijer, *Proceedings of The International Society for Optical Engineering (SPIE) (USA)*, Meeting Seattle August 2002, **4800**, 1 (2003)
- 13 J.R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Kluwer Academic/Plenum Publishers, New York 1999
- 14 A. van Dijken, A. Perro, E.A. Meulenkaamp and K. Brunner, *Organic Electronics* **4**, 131 (2004)
- 15 J. Burroughes, Society for Information Display (SID), *23rd International Display Research Conference (IDRC)*, September 2003, Phoenix, Arizona, USA, Tutorial on "Progress in Light Emitting Polymer Technology", pp. T-1/27-1/97; J.-S. Kim, P. Ho, C.E. Murphy, A.J.A.B. Seeley, I. Grizzi, J.H. Burroughes, and R.H. Friend, *Chem. Phys.*

- Lett.* **386**, 2 (2004); R.U. Khan, D.D.C. Bradly, M.A. Webster, J.L. Auld and A.B. Walker, *Appl. Phys. Lett.* **84**, 921 (2004); C. Gieberler, S.A. Whitelegg, D.G. Lidzey, P.A. Lane and D.D.C. Bradley, *Appl. Phys. Lett.* **75**, 2144 (1999)
- 16 P.W.M. Blom and M.J.M. de Jong, *IEEE J. Sel. Top. Quantum Electron.* **4**, 1077 (1998)
 - 17 M. Segal, M.A. Baldo, R.J. Holmes, S.R. Forrest, Z.G. Soos, *Phys. Rev. B* **68**, 075211 (2003); Y. Cao, I. Parker, G. Yu, C. Zhang, A. Heeger, *Nature*, 397, 414 (1999); J.-S. Kim, P.K.H. Ho, N.C. Greenham, R.H. Friend, *J. Appl. Phys.* **88**, 1073 (2000); M. Wohlgenannt, K. Tandon, S. Mazumdar, S. Ramasesha, Z.V. Vardeny, *Nature* **409**, 494 (2001); J.S. Wilson, A.S. Dhoot, A.J.A.B. Seeley, M.S. Khan, A. Köhler and R.H. Friend, *Nature* **413**, 828 (2001)
 - 18 J.C. DeMello, H.F. Wittman and R.H. Friend, *Adv. Mater.* **9**, 230 (1997)
 - 19 M. Tammer, R.W.T. Higgins and A.P. Monkman, *J. Appl. Phys.* **91**, 4010 (2002); M.-H. Lu and J.C. Sturm, *J. Appl. Phys.* **91**, 595 (2002)
 - 20 M.A. Baldo, D.F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M.E. Thompson, S.R. Forrest, *Nature* 395, 151 (1998)
 - 21 D.M. Pai, J.F. Yanus, M. Stolka, *J. Phys. Chem.* **88**, 4714 (1984)
 - 22 A. van Dijken, J.J.A.M. Bastiaansen, N.M.M. Kiggen, B.M.W. Langeveld, C. Rothe, A. Monkman, I. Bach, P. Stössel and K. Brunner, *submitted to J. Am. Chem. Soc.*; K. Brunner, A. van Dijken, H. Börner, J.J.A.M. Bastiaansen, N.M.M. Kiggen and B.M.W. Langeveld, *accepted by J. Am. Chem. Soc.*
 - 23 J.R. Justin Thomas, J.T. Lin, Y.T. Tao, C.W. Ko, *J. Am. Chem. Soc.* **123**, 94941 (2001); J.V. Grazulevicius, P. Strohriegel, J. Pielichowski, K. Pielichowski, *Prog. Polym. Sci.* **28**, 1297 (2003); S.M. Bonesi, R.J. Erra-Balsells, *J. Lumin.* 93, 51 (2001)
 - 24 A.P. Monkman, H.D. Burrows, L.J. Hartwell, L.E. Horsburgh, I. Hamblett, S. Navaratnam, *Phys. Rev. Lett.* **86**, 1358 (2001)
 - 25 T. Tsutsui, M.J. Yang, M. Yahiro, K. Nakamura, T. Watanabe, T. Tsuji, M. Fukuda, T. Wakimoto, S. Miyaguchi, *Jpn. J. Appl. Phys.* **38**, L1502 (1999); S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, H.E. Lee, C. Adachi, P.E. Burrows, S.R. Forrest, M.E. Thompson, *J. Am. Chem. Soc.* **123**, 4304 (2001)