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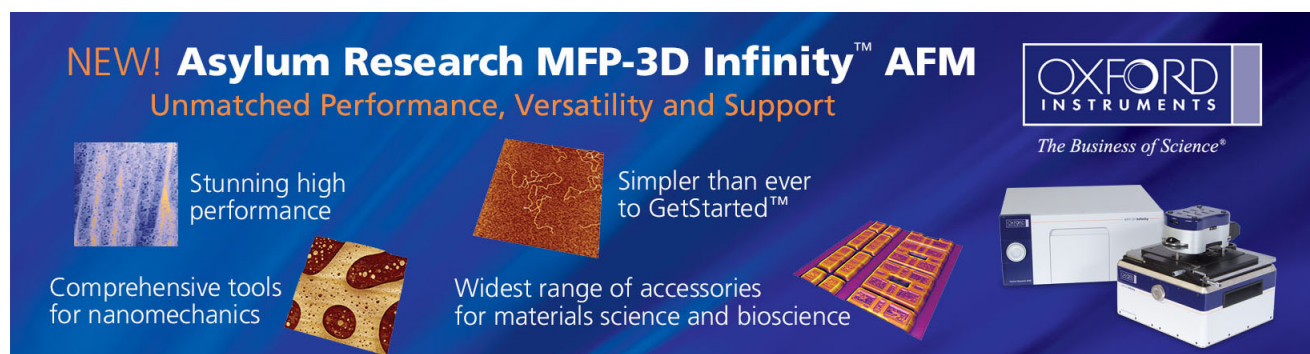
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Strong red emission in heterojunctions of conjugated polymer blends

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We demonstrate strong red electroluminescence in bilayer polymer light-emitting diodes with poly(3-hexylthiophene) and polyfluorene copolymers. The emission spectrum of the diode, peaked at 612 nm, is different from either of the two polymer layers, and is attributed to the exciplex state existing only at the heterojunction. The efficiency of this junction emission is very high for red polymer light-emitting diodes. Peak luminance of 3500 cd/m² with yield 1.3 cd/A is achieved. The emission color can be made more saturated by blending red-emitting polymers into the polyfluorene to eliminate the small residual green emission. © 2004 American Institute of Physics.

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Light-emitting diodes (LED) based on conjugated polymers cover the entire visible spectral range. Among the three primary colors, red electroluminescent polymers have the lowest efficiency. In order to realize a solution processable polymer full-color flat-panel display, high efficiency red, green, and blue LEDs are all required. Small-molecule dyes have been used as the energy-transfer dopants in the polymers to produce red emission, but the efficiency is still low.^{1,2} Another way to enhance the polymer red emission is to incorporate the triplet emitters like the iridium complexes as the dopants.^{3,4} However, solution process does not conveniently give a uniform dopant distribution and long-term stability is a problem. Recently red electroluminescent copolymers containing wide-band-gap blocks and red-emissive segments are synthesized.⁵ The LED made of blends involving such copolymers shows saturated singlet red emission with high efficiency at lower luminance of 100 cd/m². There is, however, no report of saturated red emission at high luminance (>2000 cd/m²) based on such copolymers. The difficulty with the bulk red emission from conjugated polymers, with or without doping, leads us to the alternative of heterojunction emission. There have been many reports of junction emission in bilayer polymer LEDs, in which the emission spectrum is different from the spectra of each of the two layers. The name “exciplex” is given to the interpolymer excited state responsible for the junction emission.⁶ The emission efficiency of the exciplex is, however, usually quite low.^{7,8} Exciplex emission is also present in polymer

blends.^{9–11} So far no strong red emission due to heterojunctions in either bilayer or blend is achieved. In this work we report strong red emission, peaked between 612 and 652 nm, in a series of bilayer LEDs made of poly(3-hexylthiophene) (P3HT) and polyfluorene copolymers. Peak luminance of 3500 cd/m² is achieved at 23 V with peak yield of 1.3 cd/A. Blending polyfluorene with poly(2-methoxy-5(2'-ethyl-hexyloxy)-1,4-phenylene vinylene) (MEH-PPV) or red polyfluorene copolymer further improves the color saturation. No hole-transport layer is needed for such bilayer devices.

Four devices A, B, C, and D are fabricated on cleaned indium-tin oxide (ITO) glasses. For device A (Fig. 1), a layer of P3HT from Aldrich with thickness 500 Å is spin-coated in toluene solution at 2500 rpm. The P3HT film is baked in vacuum (40 mTorr) for 100 min. A 1200 Å layer of high-

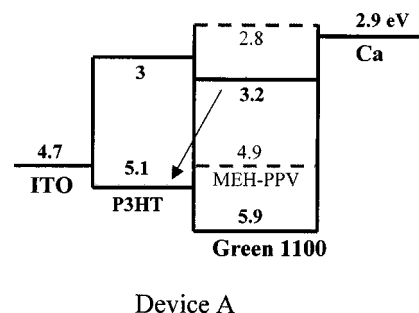


FIG. 1. The structure of device A, a bilayer polymer LED, is shown with the EA and IP of the energy bands. The heterojunction emission is indicated by an arrow. The EA and IP of MEH-PPV as a dopant are indicated by gray broken lines. Note the large hole barrier is removed by introducing MEH-PPV in Green 1100.

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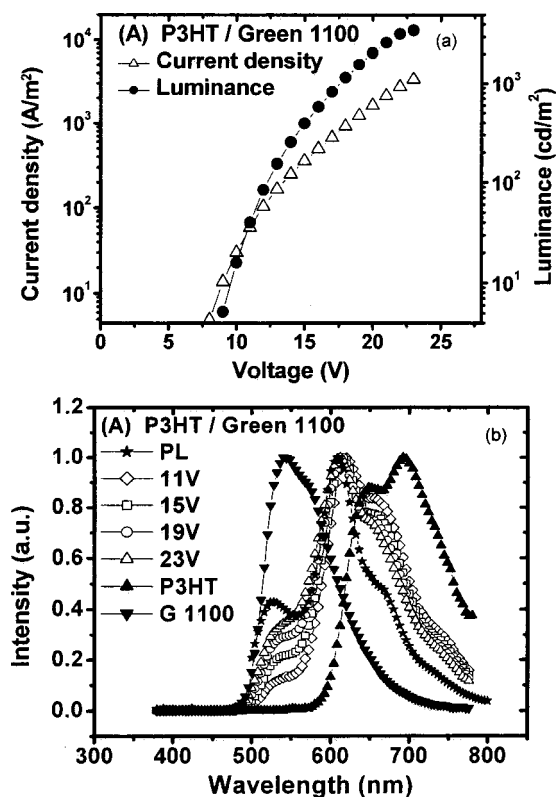


FIG. 2. (a) Current density and luminance are plotted as functions of voltage for device A. (b) Normalized PL and EL spectra for various voltages of device A are shown. EL of single-polymer LEDs made of P3HT and Green 1100 are also shown for comparison. G 1100 denotes Green 1100.

efficiency LUMATION¹² Green 1100 polyfluorene copolymer¹³ from The Dow Chemical Company Light Emitting Polymer (LEP) is then deposited over P3HT by spin-coating in toluene solution at 4000 rpm. The bilayer is baked in vacuum for 60 min. Ca/Al cathode is evaporated and the device is packaged in a glove box. The electron affinity (EA) and ionization potential (IP) of the polymers in the device are indicated in Fig. 1. For device B, the pure Green 1100 in device A is replaced by a blend of Green 1100 and LUMATION¹² Red-B polyfluorene LEP from The Dow Chemical Company.¹³ The Red-B to Green 1100 blending ratio is 9 wt %. For device C, pure Green 1100 in device A is replaced by a blend of Green 1100 and MEH-PPV with MEH-PPV to Green 1100 blending ratio 12 wt %. Device D is not a bilayer device. Instead we blend P3HT and Green 1100 to form a single-layer device, which uses poly(3,4-ethylenedioxythiophene) (PEDOT) doped with polystyrene sulphonated acid as the hole-transport layer. Note that there is no such hole-transport layer in devices A, B, and C.

The current-voltage-luminance characteristics of the P3HT/Green 1100 bilayer device A are shown in Fig. 2(a). The normalized electroluminescence (EL) spectra for various LED voltages are shown in Fig. 2(b). The EL spectra for P3HT and Green 1100 alone are shown for comparison. The spectrum of device A is dominated by an emission peaked at 612 nm, which results from neither P3HT nor Green 1100. This new emission must come from the excited state existing only between P3HT and Green 1100, i.e., an exciplex. The exciplex can be viewed as an interchain exciton whose electron is in Green 1100 and hole in P3HT. The decay of the

exciplex is indicated by an arrow in Fig. 1. The residual 540 nm shoulder due to Green 1100 is also visible in the spectra. Photoluminescence (PL) spectrum of the bilayer device is also shown. The shoulder is larger in PL than in EL. This indicates that EL is dominated by the junction while PL is determined by both the junction and the bulk. This is quite reasonable because carrier accumulation at the junction only occurs in EL. As the LED voltage increases, the maximum wavelength λ_{\max} is fixed at 612 nm. However the 540 nm shoulder rises with the voltage. The growth of the 540 nm shoulder can be understood as follows. Because of the large hole barrier of 0.8 eV between P3HT and Green 1100, virtually all the holes are blocked at P3HT side of the junction at lower voltage. Recombination only occurs when the electrons reach the junction from the Green 1100 side and form an exciplex with the holes. As the voltage increases, the strong field in the junction makes tunneling through the barrier possible and holes start to be injected into the highly luminescent Green 1100. Surprisingly even with the highest voltage the exciplex still dominates the emission despite the high efficiency of Green 1100, suggesting efficient energy transfer from the Green 1100 exciton to the exciplex. As shown in Fig. 2(a), the peak luminance of device A reaches as high as 3500 cd/m² at 23 V with yield 1.3 cd/A reached at 19 V. 100 cd/m² is reached at 12 V. While the turn-on voltage is relatively high, the peak luminance and yield are among the highest for red polymer LED with λ_{\max} longer than 600 nm. Without synthesizing any new material, these results are realized by simply combining two commercially available conjugated polymers. The 612 nm emission in device A is the strongest exciplex emission ever reported in polymer bilayer LEDs. P3HT by itself is only weakly luminescent, therefore our results demonstrate that efficient junction emission does not require both of the layers to be of high efficiency. It appears that the particular interchain morphology of these two polymers happens to give an electronic structure whose lowest interchain excited state is strongly coupled to the ground state radiatively.

The residual green 540 nm shoulder has to be removed from the spectrum in order to obtain a saturated red emission. For this purpose we add some low-energy dopants into the Green 1100, such that the excitons formed in Green 1100 could be transferred to a lower-energy excited state. In device B we add Red-B polyfluorene copolymer as the dopant into the Green 1100 host, with weight percentage of 9%. In device C, MEH-PPV is used as the dopant with weight percentage of 12%. The PL λ_{\max} for Red-B and MEH-PPV are 656 and 590 nm, respectively. The current-voltage-luminance characteristics for devices B and C are shown in Fig. 3. The normalized EL spectra are shown in Fig. 4. As expected the 540 nm shoulder is significantly reduced for both of the devices [Figs. 4(a) and 4(b)]. Unfortunately the introduction of the dopants also causes a degradation of the LED efficiency. The peak luminance of devices B and C are slightly lower than 2000 cd/m², in contrast to 3500 cd/m² of the undoped device A. The yield is reduced to less than half of device A (1.3 cd/A). The maximum yield is 0.61 cd/A (18 V) for device B, and 0.43 cd/A (18 V) for device C. Device B is the best in terms of emission color. λ_{\max} is at 652 nm while the Commission Internationale de L'Eclairage (CIE)

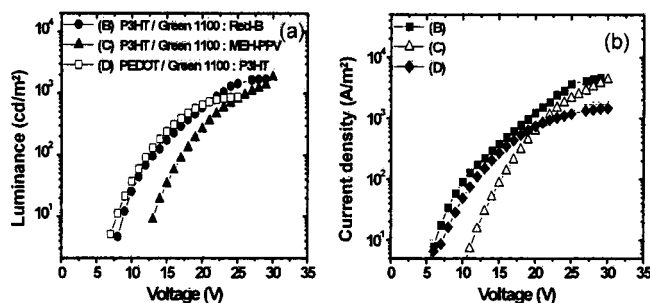


FIG. 3. Current density and luminance of devices B, C, and D are plotted as functions of voltage.

coordinate is (0.64, 0.35) (saturated red) at 100 cd/m². The performance of device B is among the best for saturated red polymer LEDs. One of the possible reasons for the efficiency degradation of devices B and C is that the large hole energy barrier at the junction is removed by the dopants, as indicated by the broken gray lines in Fig. 1. The IP of the red emitting Red-B and MEH-PPV are much smaller than Green 1100, so the holes can easily go through the junction and there is no longer a large number holes accumulated at the junction to form the exciplex. In addition to bilayer devices, we also fabricated single-layer device with Green 1100 blended with P3HT (6 wt %) as the emissive layer. Similar to the bilayer devices the EL spectrum is dominated by the exciplex. The yield is not low (0.9 cd/A), but the peak luminance is further reduced to 870 cd/m². The hole distribution in the single-layer blend is expected to be more uniform than in the bilayers. Combining the results of bilayer and single-layer blend we conclude that the spatial accumulation of holes at the junction is necessary for the efficient exciplex emission. The performance for devices A–D are summarized in Table I. In addition to the red LEDs, we also made a nearly white LED by adding a layer of blue emitting poly(9,9-dioctylfluorene-2,7-diyl) (PFO) between Green 1100 and Ca/Al. Red, green, and blue emissions come from the exciplex, Green 1100, and PFO, respectively. The EL spectrum is shown in Fig. 4. The peak luminance is 150 cd/m². Such LED can be easily integrated with a P3HT field-effect transistor¹⁴ to form an active pixel for full-color polymer displays.

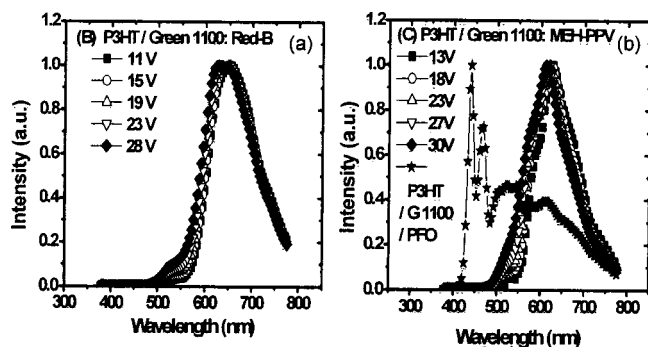


FIG. 4. The normalized emission spectra for devices B, C, and D are shown for various voltages. Note the green 540 nm shoulder is reduced in comparison with device A. Triple-layer device (star sign) is also shown. G 1100 denotes Green 1100.

TABLE I. The performance of all the devices are summarized. The luminance and yield are peak values. λ_{\max} is at the peak luminance.

Device	Yield (cd/A)	Luminance (cd/m ²)	λ_{\max} (nm)	CIE at 100 cd/m ²
A	1.3	3500	612	(0.59, 0.40)
B	0.61	1720	628	(0.64, 0.35)
C	0.43	1871	612	(0.60, 0.40)
D	0.90	869	612	(0.59, 0.40)

The CIE coordinate for device A deviates from the saturated red because of the emergence of the small green shoulder with the increasing voltage. The strong red emission itself does not spectrally shift with the voltage. The dominant emission at 612 nm with peak luminance 3500 cd/m² is very high for singlet red emission in conjugated polymers. Surprisingly it comes from the exciplex at the junctions instead of exciton in the bulk. It is interesting to note that no hole-transport layer like PEDOT is used between ITO and P3HT for such a high efficiency LED. This is because the hole injection barrier between ITO and P3HT is small.

In conclusion, strong red emission is obtained from junctions of bilayer LEDs made of P3HT and green polyfluorene copolymers. Our results open a possibility to overcome the difficulty in synthesizing new polymers for red emission by the exciplex emission at the heterojunction between existing polymers.

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