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Control of color and efficiency of light-emitting diodes based on polyfluorenes blended with hole-transporting molecules

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Adding low-molecular-weight hole-transporting molecules (HTM) with different oxidation potentials to the polyfluorene emission layer of single-layer light-emitting diodes causes significant changes in the device properties. The pronounced increase in luminance efficiency combined with a decrease in current is attributed to significant hole trapping, as further suggested by thermoluminescence experiments. Using a oligo-triphenylamine HTM with an ionization potential of ~4.9 eV, light-emitting diodes with stable blue emission, a brightness of 800 cd/m^2 and an efficiency of 0.87 cd/A were realized. Further, the red-emitting contribution to the spectra as observed in the pure polymer devices could be fully suppressed. © *2000 American Institute of Physics.* [S0003-6951(00)05214-1]

Organic light-emitting diodes (OLEDs) have received considerable attention both in academic research and industrial development due to their processibility and achievable efficient conversion of electrical power into light output.[1–3] Performance of the devices is significantly influenced by the charge balance between electrons and holes since the excess of one type over the other leads to an increase in current but no emission contribution.[4] Another factor consequential to the efficient luminescence is aggregate formation resulting in a reduction of the radiative recombination efficiency and redshifted emission bands.[5] In polyfluorene (PF) homopolymers such redshifted emission bands are frequently observed in electroluminescence (EL) and photoluminescence (PL).[6–9] Either the formation of aggregates/excimer[7,8] or the degradation of the polymers during operation of the LED has been proposed.[9] In our effort to fabricate LEDs with strongly linearly polarized emission, we have synthesized PFs with different side chain patterns, some of which show redshifted emission already for the freshly prepared LED.[10,11] Here, we demonstrate that the addition of deep hole traps at low concentration leads to a stable blue emission and at the same time significantly improves the device efficiency and brightness.

Single layer OLEDs were prepared from poly(2,7-(9,9-bis(2-ethylhexyl))co-(9,9-bis((3S)-3,7-dimethyloctyl)) fluorene) (PF C26) and its blends with several low-molecular-weight hole-transporting molecules (HTMs)—a triphenylamine derivative (TPTE),[12] starburst amine (ST 755) and N,N'-diphenyl-N,N'-bis-α-naphtylbenzidide (ST 16/7) at weight ratio 1 to 0.03. PF C26 was synthesized as described elsewhere.[10] ST 755 and ST 16/7 were purchased from SynTec GmbH - SYNTHON AcMaRi Chemie GmbH & Co. KG, Germany. All devices were fabricated at ambient conditions by spin coating the polymer–HTM solution in toluene onto glass substrates covered by patterned indium–tin–oxide electrodes and a 25 nm layer of polyethylenedioxythiophene doped with poly(styrene sulfonate) (PEDT:PSS). Samples were dried in vacuum at room temperature for 24 h prior to the evaporation of Ca/Al top electrodes. Typical emission layer thicknesses (as measured with a Tencor α-step profiler) were 90 nm. The overlap between the two electrodes resulted in device areas of 5 mm^2. The device characterization was carried out in an evacuated sample chamber.

The current–voltage characteristics of the devices as measured with a Keithley 236 source-measure unit are presented in Fig. 1. Compared to the pure PF C26 the current density is decreased in the case of blend emission layers. This effect was comparable or even better pronounced in other PF hosts. Based on the energy level scheme in Fig. 2, all HTMs will act as hole traps, while not affecting electron transport to a large extent. It has been shown that addition of dopands with lower oxidation potential at a concentration of a few percent leads to a drastic decrease in hole drift mobility.[13] More important, trapping of holes will cause a space charge field, which adds to the applied external field. As a consequence the total electric field is reduced at the anode and enhanced at the cathode.[14] If the current through the device is affected by charge carrier injection, as indicated by the energy diagram in Fig. 2, this additional field will moreover aggravate the injection of holes while facilitating

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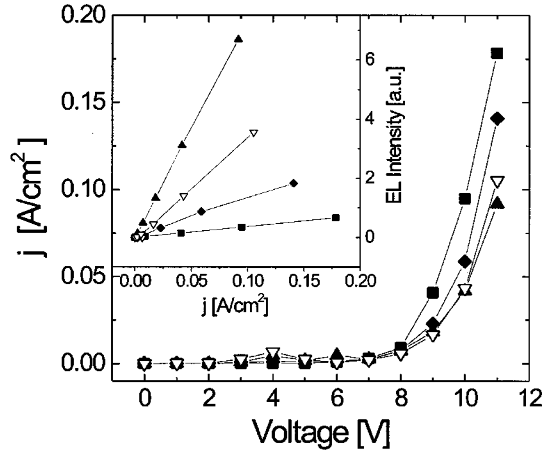

FIG. 1. Current–voltage characteristics of the LEDs based on polyfluorene and its blends with different HTMs: pure PF C26 (■), PF C26+TPTE (▲), PF C26+ST 755 (◆), and PF C26+ST 16/7 (∇), at a concentration of the HTM of 3 wt %. The inset shows the luminance vs current characteristics.

the injection of electrons, thus improving the carrier balance. This interpretation is supported by the luminance-versus-current density dependence of the devices (Fig. 1, inset). In all cases, addition of the HTMs enhances the efficiency compared to the pure PF C26 devices. As the current decreases and the luminance efficiency increases upon addition of the HTMs, we propose that the current in the configuration with PEDT is hole dominated and that the emission intensity is limited by electron injection. These observations are in agreement with conclusions by Pommerehne *et al.*[15] that the enhancement of efficiency due to a reduced mobility of one of the charge carriers is most prominent if this carrier is injected through the lower barrier. Previous investigations of the same doped layers in devices without PEDT:PSS showed a decrease in onset voltage for both current and emission in comparison with pure polyfluorene. In this case, hole injection seems to be the limiting process for the overall device performance.

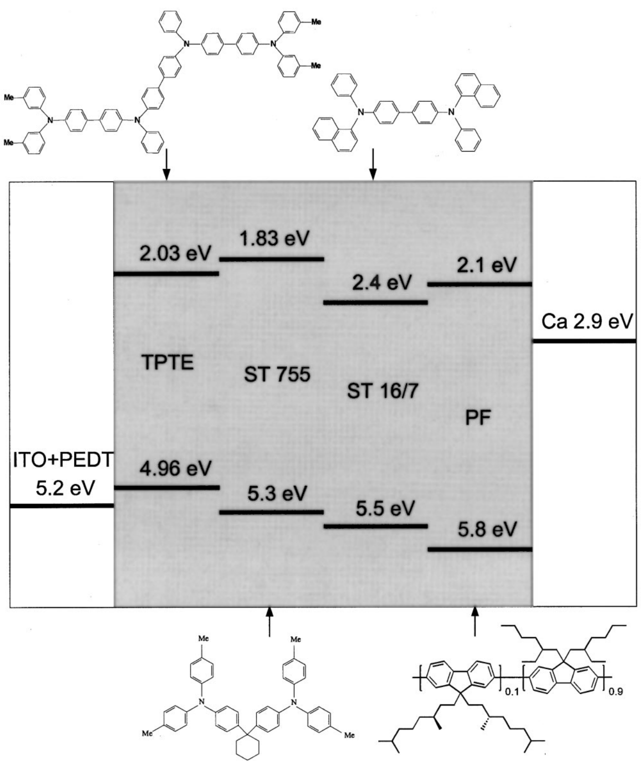

FIG. 2. Chemical structure and energy level diagrams of the used compounds. Highest occupied molecular orbital (HOMO) levels of ST 755, ST 16/7 and PF (Ref. 23) were determined from cyclic voltammetry (CV) measurements and in the case of TPTE by X-ray photoelectron spectroscopy (XPS) (Ref. 12). The PEDT:PSS work function was taken from Ref. 24. The lowest unoccupied molecular orbital (LUMO) level position of PF was also estimated via CV and the optical gap was found to be 2.95 eV. For all the other compounds the LUMOs were calculated by adding the optical band gap to the HOMO values, which underestimates the true HOMO–LUMO distance.

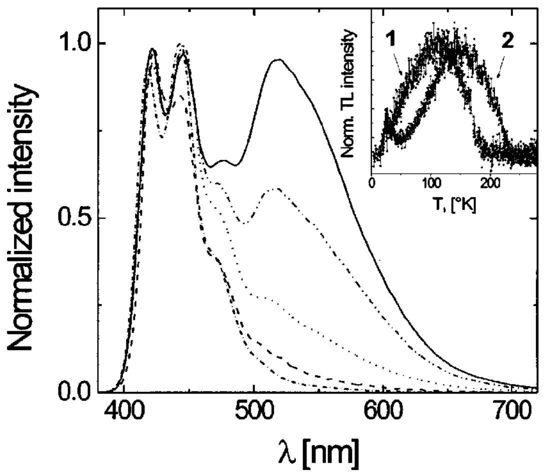

FIG. 3. EL spectra of the different layers: PF C26 (—), PF C26+TPTE (−−), PF C26+ST 16/7 (·····), PF C26+ST 755 (-···-). Also shown is the PL spectrum of PF C26 (-·-·). The inset shows the normalized thermoluminescence (TL) glow curves of pure PF C26 (curve 1) and blended with 3 wt % TPTE (curve 2), recorded at a heating rate of 7 K/min.

Addition of the HTMs significantly affects the EL spectra as displayed in Fig. 3. Three main peaks can be identified: exciton emission at ~425 and 448 nm and a broad band at ~527 nm. Upon blending the peak positions are not changed but the blue excitonic emission bands representing the inherent characteristics of polyfluorenes become far more pronounced. For comparison, the spectral shape of the corresponding PL spectra remained almost unchanged. Note that similar effects, but to a much weaker extent, have been observed in a ladder type poly(*p*-phenylene),[16] which has an oxidation potential of 5.5 eV.

In the following we want to outline a mechanism for the observed increase in blue emission intensity upon addition of HTMs based on hole trapping. As the red emission contribution is already observed when turning on the freshly prepared devices, its origin cannot be related to device degradation. Also, its relative intensity in EL is much higher than in PL, suggesting that the species causing it are already present in the ground state and predominately populated due to charge carrier trapping.[17] Due to the low ionization potential, the HTMs might compete with these sites with respect to hole trapping in the blend emission layer. Those holes might eventually became detrapped and recombine with an electron on a nearby PF chain, provided that the HTMs are molecularly dispersed in the PF layer. Interestingly, the spectral changes are far less pronounced and less reproducible in case of the starburst-type ST 755, even though its influence on the current and emission intensity is clearly visible. Similar effects have been observed for another starburst-type HTM-

TABLE I. EL efficiency, brightness and CIE color coordinates (measured with a spot photometer (MINOLTA CS-100) of devices with blend emission layers for a HTM concentration of 3 wt. %, compared to a pure PF C26 device at a driving voltage of 11 V.

Dopand	None	TPTE	ST 755	ST 16/7
Luminance (cd/m^2)	70	800	110	160
Efficiency (cd/A)	0.04	0.87	0.08	0.15
x	0.283	0.166	0.187	0.176
y	0.366	0.126	0.163	0.128

(SynTec ST 638). Most likely the nonplanar shape of the molecules reduces the compatibility with the rod-like polyfluorenes, leading to phase separation phenomena.

The interpretation that the introduction of HTMs modifies the charge carrier trapping is further supported by thermoluminescence (TL) experiments, which are known to be very sensitive to carrier trapping effects.[18,19] Upon addition of TPTE the maximum of the TL shifts to higher temperatures by ~50 K, which clearly indicates the introduction of deeper trapping sites (Fig. 3, inset).

The performances of the light emitting diodes (LEDs) are summarized in Table I. For all blend devices, the color coordinates of emission remained stable during device characterization. Blends with TPTE exhibit the highest brightness up to 800 cd/m^2 and the highest efficiency. The value 0.87 cd/A exceeds the efficiency of a bilayer device with a similar PF homopolymer including a TPD hole transport layer (0.25 cd/A)[1] and of a bilayer structure based a thermally crosslinked polyfluorenes (~0.2–0.3 cd/A).[20] In the latter example the efficiency could be further enhanced by adding an appropriate electron transporting layer.

In conclusion, addition of molecules with low oxidation potentials to a polyfluorene is shown to lead to stable blue electroluminescence and to an increase in device efficiency. The results have been attributed to efficient hole trapping. While charge carrier trapping has been attributed to the pronounced enhancement of the efficiency in electroluminescence[21] and electrophosphorescence[22] with emissive dopands, our results indicate that the addition of nonradiative molecules with appropriate energy levels can significantly improve the LED device performance.

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