Polybenzobisazoles Are Efficient Electron Transport Materials for Improving the Performance and Stability of Polymer Light-Emitting Diodes

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A series of seven polybenzobisazoles were investigated as electron transport materials in arylene vinylene polymer-based electroluminescent devices. A large enhancement in performance and stability was observed in poly(*p*-phenylene vinylene) and poly(2-methoxy-5(2′-ethyl-hexyloxy)-1,4-phenylene vinylene) light-emitting diodes by using polybenzobisthiazoles and poly(*p*-phenylene benzobisoxazole) as electron-transport materials. Devices using polybenzobisazole electron transport layers and aluminum cathodes had a turn-on voltage as low as 2.8 V, a luminance of up to 1400 cd/m^2, and an external quantum efficiency of up to 2.5%. These polymer devices and their performances were stable under repeated testing over a period of 9−10 months storage in air. The superior performance of the polybenzobisazole thin films as electron-transport and hole-blocking materials in polymer light-emitting diodes is due to their high glass-transition temperature, environmental resistance, and photochemical/electrochemical stability. These results demonstrate that robust high-temperature polybenzobisazoles can be used as efficient electron-transport and hole-blocking materials for improving the performance and stability of polymer light-emitting devices.

Introduction

Polymer light-emitting devices are currently being explored in large-area flat-panel color displays.[1,2] Arylene vinylene polymers such as poly(*p*-phenylene vinylene) (PPV) and poly(2-methoxy-5(2′-ethyl-hexyloxy)-1,4-phenylene vinylene) (MEH-PPV) have been most widely investigated as the emissive materials in light-emitting diodes (LEDs).[1−4] Because arylene vinylene polymers and most of the other emissive materials used in the construction of polymer LEDs (e.g., polythiophene,[1] poly(*p*-phenylene)s,[4a] and polyfluorenes[2a,5]) have relatively poor electron-accepting and -transporting properties, single-layer devices have poor performance due to these poor electron-injection and -transport qualities. Oxadiazole molecules and polymers have been widely used as electron-injection and -transport materials to improve the performance of polymer LEDs.[1,3] However, their performance as electron-transport materials has been inadequate.[3,6,7] For example, polymer LEDs incorporating oxadiazole molecules and polymers as electron-transport materials generally have high operating voltages.[3,6,7] Low glass-transition temperature (T_g) of electron-transport materials used in polymer LEDs has been identified as an important source of device instability.[3] A few recent studies have explored *n*-type conjugated polymers, such as polyquinolines,[2b,8] poly-(quinoxaline)s,[9] and polypyridine[10] as electron-transport layers in polymer LEDs. One of the major current challenges to improving the performance, stability, and durability of polymer LEDs is the development of photochemically and thermally robust electron-transport materials.

In this paper, we report the use of polybenzobisazoles as electron-transport materials for polymer LEDs. The conjugated rigid-rod polybenzobisazoles (PBZs, Chart 1), which have been extensively studied in our laboratory, combine robust high-temperature resistance with photo-

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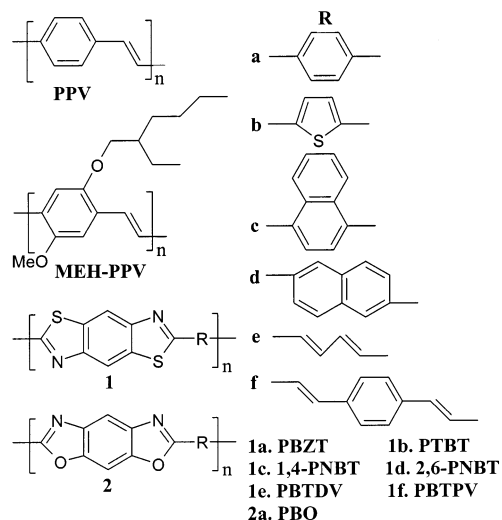
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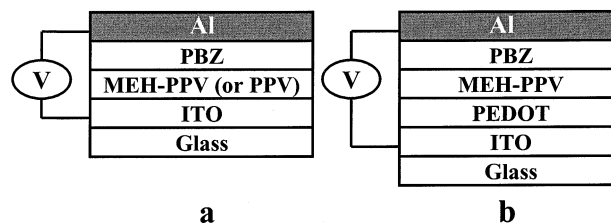
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**Chart 1. Chemical Structures of
Polybenzobisazoles, MEH-PPV, and PPV**

1a. PBZT   1b. PTBT
1c. 1,4-PNBT 1d. 2,6-PNBT
1e. PBTDV   1f. PBTPV
2a. PBO

Figure 1. Schematic of polymer LED structures.

chemical and electrochemical stability, *n*-type dopability, and solution processability by spin coating.[11−17] When the PBZs were used as electron-transport materials for MEH-PPV- and PPV-based LEDs, the resulting electroluminescent (EL) devices had low turn-on voltage, high external quantum efficiency, high luminance levels, and substantial air stability.

We explored the use of the polybenzobisazoles as electron-transport materials in polymer LEDs because of their combination of *n*-type (electron accepting) and other physicochemical properties.[11−14] Efficient π-stacking and strong intermolecular interactions underly their high T_g (>400−500 °C), high-temperature resistance, excellent mechanical properties, photochemical stability, and insolubility in common organic solvents.[11−14] The π-stacking of these aromatic heterocyclic polymers[18] also lead to their ready formation of excimers and poor fluorescence efficiency in the solid state.[14,17] Recently, the field-effect mobility of *electrons* in poly(*p*-phenylenebenzobisthiazole) was estimated from thin film transistors and found to be 2×10^{-7} cm²/V.[19] This electron mobility is on the same order of magnitude as the *hole* mobility in MEH-PPV and PPV ($\sim 10^{-7} − 10^{-6}$ cm²/V),[20] suggesting good prospects of balanced charge transport in arylene vinylene polymer LEDs incorporating polybenzobisazoles.

Experimental Section

Materials. All the polybenzobisazoles (Chart 1) used in this study were previously synthesized in our laboratory. Their synthesis, characterization, and electrochemical, optical, and nonlinear optical properties were previously reported.[11−17] The sulfonium precursor of poly(*p*-phenylene vinylene) (PPV) in ~1 wt % methanol solution, poly(2-methoxy-5(2′-ethyl-hexyloxy)-1,-4-phenylene vinylene) (MEH-PPV, $M_w \sim 85\,000$), and poly-(ethylenedioxythiophene)/poly(styrenesulfonic acid) (PEDOT/PSS) solution in water were purchased from Lark Enterprises, American Dye Source, Inc., and Aldrich Chemical Co., respectively. All solvents were of spectroscopic grade and were used as received.

The names and abbreviations of the polybenzobisazoles used are as follows: poly(*p*-phenylenebenzobisthiazole) (PBZT, **1a**); poly(2,5-thienylenebenzobisthiazole) (PTBT, **1b**); poly(1,4-naphthalenebenzobisthiazole) (1,4-PNBT, **1c**); poly(2,6-naphthalenebenzobisthiazole) (2,6-PNBT, **1d**); poly(divinylene-benzobisthiazole-2,6-diyl) (PBTDV, **1e**); poly(1,4-phenylene divinylenebenzobisthiazole) (PBTPV, **1f**); and poly(*p*-phenylenebenzobisoxazole) (PBO, **2a**).

Fabrication of Polymer LEDs. Schematic structures of the polymer LEDs are shown in Figure 1. In the devices, indium−tin oxide (ITO) was used as the anode, PPV or MEH-PPV was used as the emissive layer, each of the various conjugated polybenzobisazoles (**1a−f**, **2a**, as shown in Chart 1) was used as an electron transport (*n*-type) layer, and aluminum (Al) was used as the cathode.

The LEDs were fabricated by sequential spin coating of the polymer layers onto a pre-cleaned ITO-coated glass substrate. MEH-PPV thin films were spin coated from a 0.5 wt % solution in CHCl₃ onto ITO and dried at 60 °C in a vacuum for 8 h. PPV thin films were spin coated onto ITO from a sulfonium precursor solution in methanol, followed by thermal conversion in a vacuum at 250 °C for 1.5 h.[2b] Thin films of a polybenzobisazole, such as PBZT, were spin coated from a 0.3 wt % solution in methanesulfonic acid (MSA) onto the MEH-PPV (or PPV) layer and immersed in deionized water for 12−14 h to remove the MSA solvent. The bilayer thin films were dried in a vacuum at 60 °C for 10 h before vapor deposition of the aluminum electrode under high vacuum ($\sim 3 \times 10^{-6}$ Torr). In some devices, a thin layer of poly(ethylenedioxythiophene)/polystyrenesulfonate (PEDOT) (<40 nm) was first spin coated from its solution in water onto ITO and dried at 80 °C in a vacuum for 10 h. Then, MEH-PPV and polybenzobisazole layers were sequentially spin coated as described above. The film thicknesses were measured by an Alpha-step profilometer (model 500, KLA Tencor, San Jose, CA) with an accuracy of ±1 nm and confirmed by an optical absorption coefficient technique. A 100-nm-thick aluminum layer was thermally deposited to form an active diode area of 0.2 cm² (5-mm diam).

Characterization of LEDs. Electroluminescence (EL) and photoluminescence (PL) spectra were measured on a SPEX Fluorolog-2 spectrofluorimeter. The electrical characteristics of the devices were measured on an HP4155A semiconductor parameter analyzer together with a Grasby S370 optometer equipped with a calibrated luminance sensor head.[2b,8] The EL

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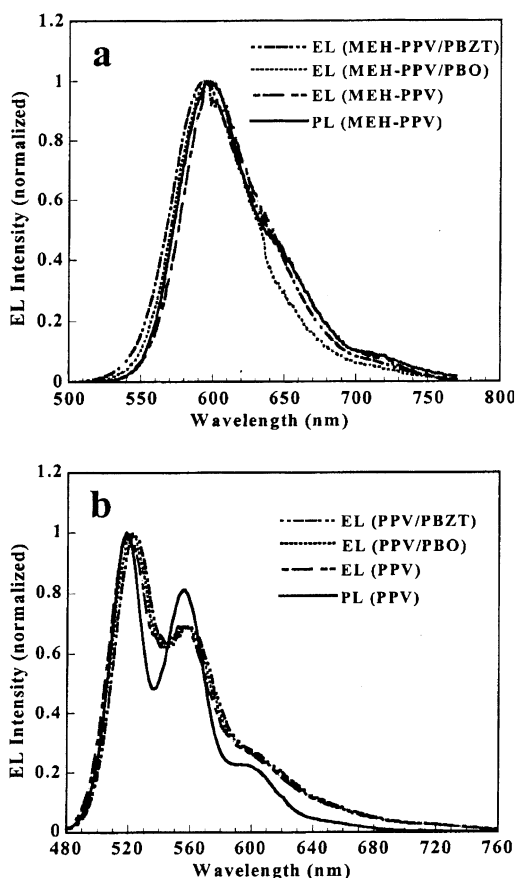
Figure 2. Normalized EL spectra of (a) MEH-PPV-based LEDs and (b) PPV-based LEDs. The thin film PL spectra of MEH-PPV and PPV are also shown.

quantum efficiencies of the diodes were measured by using procedures similar to those previously reported.[2b,8] All the fabrication and measurements were done under ambient laboratory conditions.

Results and Discussion

The EL emission from all the MEH-PPV/PBZ diodes, such as ITO/MEH-PPV(45 nm)/PBZT(35 nm)/Al and ITO/MEH-PPV(45 nm)/PBO(30 nm)/Al, was orange−red (λ_{max} = 585 nm) and identical with that of the single-layer MEH-PPV diode at all forward bias voltages (Figure 2a). This shows that the emission zone of these polymer LEDs is located in the MEH-PPV layer. Similar orange−red EL emission was also observed from devices incorporating a thin-layer of PEDOT (<40 nm) at all forward bias voltages. Figure 2b shows the EL spectra of the PPV-based devices such as ITO/PPV(30 nm)/PBZT(35 nm)/Al, ITO/PPV(30 nm)/PBO(30 nm)/Al, and ITO/PPV(30 nm)/Al. The EL emission from all PPV/PBZ diodes was green ($\lambda_{max} \sim$ 515 nm) at all forward bias voltages and identical with that of the single-layer PPV diode. These observations imply that the emitting excited-state species was generated in the MEH-PPV (or PPV) layer. These EL spectral results also suggest that the polybenzobisazole layer functions as an electron-transport and a hole-blocking material in the devices.

Representative current−voltage and luminance−voltage curves of MEH-PPV-based LEDs are shown in Figure 3 parts a and b. The single-layer ITO/MEH-PPV-(45 nm)/Al diode had a turn-on voltage of 12 V and a luminance of 163 cd/m² at 15.5 V and a current density
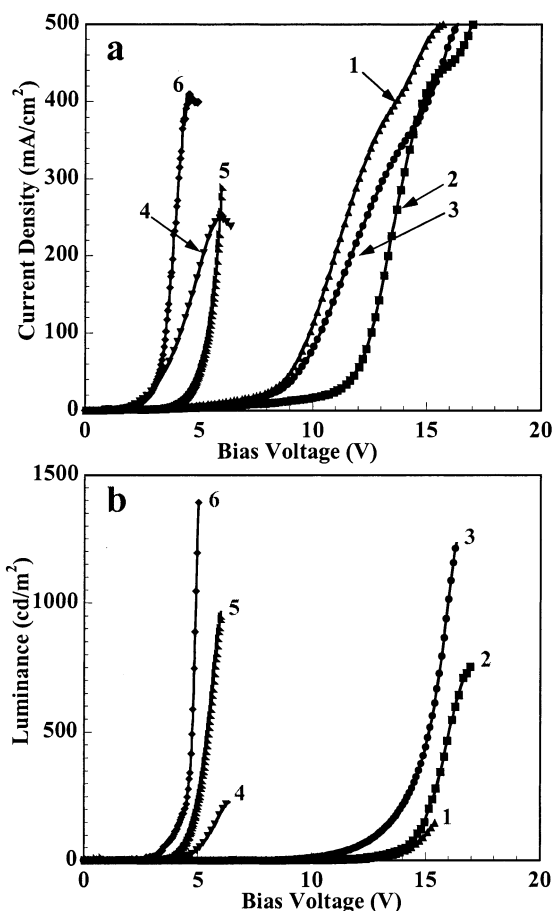

Figure 3. (a) Current−voltage and (b) luminance−voltage curves of MEH-PPV-based LEDs: (1) MEH-PPV, (2) MEH-PPV/PBO, (3) MEH-PPV/PBZT, (4) PEDOT/MEH-PPV, (5) PEDOT/MEH-PPV/PBO, and (6) PEDOT/MEH-PPV/PBZT.

Table 1. Summary of Performance of ITO/MEH-PPV/PBZ/Al LEDs

device	V_{on} V	J_{max} mA/cm²	L_{max} cd/m²	V_{max} V	Φ_{ext} %
MEH-PPV	12	500	163	15.5	0.02
MEH-PPV/2,6-PNBT	8	500	354	11.0	0.08
MEH-PPV/1,4-PNBT	7	500	266	11.0	0.07
MEH-PPV/PBZT	6	500	1250	16.0	0.28
MEH-PPV/PBO	7	500	777	17.0	0.15
MEH-PPV/PBTPV	7.5	338	243	19.5	0.05
MEH-PPV/PBTDV	6.5	287	207	11.5	0.10
MEH-PPV/PTBT	8.5	500	187	13.0	0.04

of 500 mA/cm². The bilayer ITO/MEH-PPV(45 nm)/ PBZT(35 nm)/Al diode showed bright orange−red EL emission with a turn-on voltage of 6 V and a luminance of 1250 cd/m² at 16 V and a current density of 500 mA/ cm² (Table 1). From the bilayer ITO/MEH-PPV(45 nm)/ PBO(30 nm)/Al diode, similar bright orange−red EL emission was observed with a luminance of 777 cd/m² at 17 V. The bilayer LEDs using PBZT or PBO as an electron-transport layer operated at a reduced turn-on voltage compared to that of the single-layer MEH-PPV diode. The turn-on voltages (V_{on}) for other PBZ bilayer LEDs were also less than that of the single-layer MEH-PPV diode (Table 1), suggesting improved electron injection and transport compared to that of the single-layer MEH-PPV diode. The luminance of the bilayer LEDs using a PBZ as an electron-transport layer was also substantially enhanced compared to that of the single-layer MEH-PPV diode, as exemplified in Figure

**Table 2. Summary of Performance of
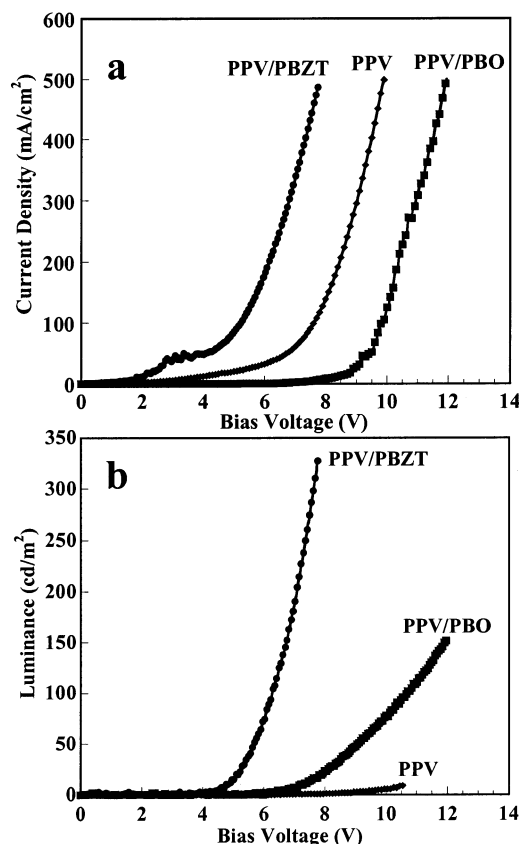ITO/PEDOT/MEH-PPV/PBZ/Al LEDs**

device	V_{on} V	J_{max} mA/cm^2	L_{max} cd/m^2	V_{max} V	Φ_{ext} %
MEH-PPV	3.8	238	220	6.5	0.3
MEH-PPV/2,6-PNBT	3.2	394	561	8.0	0.56
MEH-PPV/1,4-PNBT	3.1	386	587	7.5	0.65
MEH-PPV/PBZT	2.8	411	1400	5.0	2.5
MEH-PPV/PBO	2.9	290	970	6.0	1.9
MEH-PPV/PBTPV	3.2	343	433	8.0	0.49
MEH-PPV/PBTDV	3.1	297	429	8.5	0.55
MEH-PPV/PTBT	3.3	328	397	8.0	0.46

3b. The luminance values of the MEH-PPV/PBZT and MEH-PPV/PBO diodes were 1250 and 777 cd/m^2, respectively. These luminance values are factors of 5−8 times greater than that of the single-layer MEH-PPV diode. Enhancement of device luminance was also observed for bilayer LEDs using other polybenzobisazoles (Table 1).

The performance data of bilayer MEH-PPV/PBZ LEDs, including the turn-on voltage (V_{on}), maximum luminance (L_{max}) with corresponding operating voltage (V_{max}), current density (J_{max}), and external quantum efficiency (Φ_{ext}) are summarized in Table 1. The reference external quantum efficiency of the single-layer MEH-PPV diode was 0.02%. The external quantum efficiency of bilayer MEH-PPV devices vary from 0.04 to 0.28% depending on the specific polybenzobisazole used as an electron-transport layer. The bilayer MEH-PPV/PBZT and MEH-PPV/PBO diodes had the highest external quantum efficiencies of 0.28 and 0.15% (photons/electron), respectively. This represents a factor of 8−14 enhancement compared to the single-layer MEH−PPV diode. Incorporation of a polybenzobisazole as an electron-transport layer has thus resulted in a large improvement in the performance (lower turn-on voltage, higher luminance, and higher EL efficiency) of MEH-PPV-based LEDs.

The performance of LEDs of the type ITO/PEDOT/MEH-PPV/PBZ/Al was also investigated. The external quantum efficiency of ITO/PEDOT/MEH-PPV(45 nm)/Al diode was 0.3% with a maximum light output of 220 cd/m^2 at 6.5 V and a turn-on voltage of 3.8 V (Table 2). As shown in Table 2, all the LEDs incorporating a polybenzobisazole electron-transport layer have enhanced performance compared to that of the reference PEDOT/MEH-PPV device. The ITO/PEDOT/MEH-PPV/PBZT/Al diode showed the best performance with an external quantum efficiency of 2.5% and a maximum brightness of 1400 cd/m^2 at 5 V and a turn-on voltage of 2.8 V. For ITO/PEDOT/MEH-PPV/PBO/Al diode, a turn-on voltage of 2.9 V and a luminance of 970 cd/m^2 at 6 V with an external quantum efficiency of 1.9% were achieved. On the basis of the external quantum efficiency of LEDs, the decreasing order of effectiveness as an electron transport layer among the polybenzobisazoles is: PBZT > PBO > 1,4-PNBT > 2,6-PNBT > PBTDV > PBTPV > PTBT.

The use of polybenzobisazoles as electron-transport materials for PPV-based LEDs was also investigated. Figure 4a shows the current−voltage curves of two representative bilayer LEDs (PPV/PBZT and PPV/PBO) and the single-layer PPV diode. The corresponding luminance−voltage curves for these LEDs are shown in Figure 4b. The current through the devices showed

Figure 4. (a) Current−voltage and (b) luminance−voltage curves of PPV-based LEDs.

**Table 3. Summary of Performance of
ITO/PPV/PBZ/Al LEDs**

device	V_{on} V	J_{max} mA/cm^2	L_{max} cd/m^2	V_{max} V	Φ_{ext} %
PPV	8.5	500	10	10.5	0.002
PPV/2,6-PNBT	8	500	77	14.5	0.02
PPV/1,4-PNBT	7.5	120	50	10.5	0.05
PPV/PBZT	4	500	340	7.7	0.24
PPV/PBO	6	500	153	12.0	0.12
PPV/PBTPV	7.5	500	33	14.5	0.006
PPV/PBTDV	8.5	500	27	15.0	0.004
PPV/PTBT	7	370	22	10.7	0.008

characteristic diode field dependence. Bright green EL emission with turn-on voltage of 4 V and a luminance of 340 cd/m^2 at 7.7 V were observed for the ITO/PPV-(30 nm)/PBZT(35 nm)/Al diode. In contrast, the single-layer PPV diode had a turn-on voltage of 8.5 V and a luminance of 10 cd/m^2 at 10.5 V with a current density of 500 mA/cm^2 (Table 3). A turn-on voltage of 6 V and a luminance of 153 cd/m^2 at 12 V were observed for ITO/PPV(30 nm)/PBO(30 nm)/Al diode. The external quantum efficiency of the single-layer PPV diode was only 0.002%, whereas those of the two best PPV/PBZ diodes were 0.12−0.24%. The external quantum efficiency is thus enhanced by a factor of 60−120 times when PBO and PBZT electron-transport layers are used instead of the single-layer PPV diode. Improvement in performance of PPV-based LEDs was also observed when other polybenzobisazoles were used as the electron-transport layer (Table 3). The enhanced performance (lower turn-on voltage, higher luminance, and higher EL efficiency) of these bilayer LEDs using polybenzobisazole as the electron-transport layer implies im-
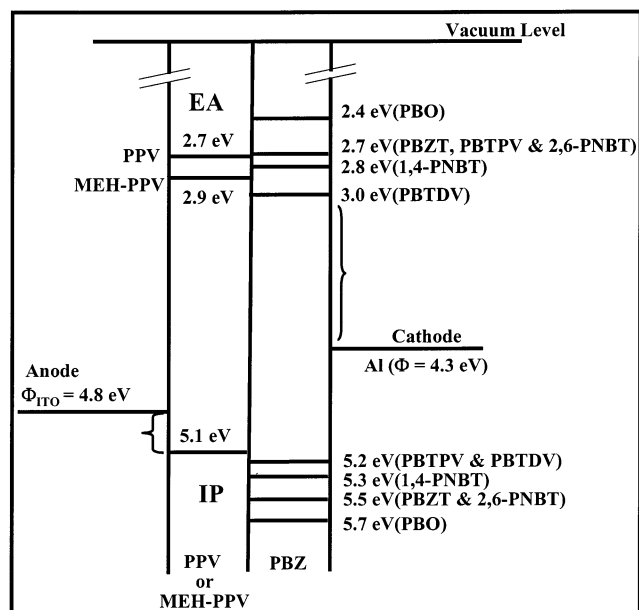
Figure 5. Schematic energy diagram of MEH-PPV(or PPV)/ polybenzobisazole EL diodes.

proved electron injection and transport compared to that of the single-layer PPV diode.

The HOMO/LUMO energy levels[12] and electrode work functions[8b] of the polymer LEDs investigated are shown in Figure 5 as a means to understanding why the polybenzobisazoles facilitate good device performance. From the HOMO energy levels, all the polybenzobisazoles thus have excellent hole-blocking properties relative to either MEH-PPV or PPV. However, on the basis of the LUMO energy levels which are either comparable to or higher-lying than those of MEH-PPV and PPV, there is a large barrier of about 1.3−1.9 eV to electron injection from aluminum electrode into the polybenzobisazoles. In fact, the barrier to electron injection is larger than that in the ITO/MEH-PPV/Al single-layer diodes (HOMO/LUMO = 5.1/2.9 eV)[21] and comparable in size to that of single-layer PPV diodes (HOMO/LUMO = 5.1/2.7 eV)[2b] which have poor LED performance.[1,2b,7,8,10] A reaction at the aluminum−polybenzobisazole interface may substantially reduce or eliminate this barrier, facilitating electron injection in these polybenzobisazole LEDs as proposed earlier for polyquinoline LEDs.[2b,8] Formation of such an aluminum−polybenzobisazole complex could explain all the experimental data, particularly why all the polybenzobisazoles, regardless of their LUMO levels, facilitate efficient electron injection. Although we do not have direct evidence of the aluminum−polybenzobisazole interface reaction, extensive surface spectroscopic studies of other metal−conjugated polymer interfaces suggest the generality of such reactions which are especially facilitated by the presence of electron-rich atoms in the polymers.[22] Our own prior studies of various heterocyclic polymers, including the polybenzobisazoles, have established the facile coordination complexation of metal halide Lewis acids (e.g., AlCl₃) to the heteroatom

sites.[11c,13] Similar Al atom complexation reaction starting at the imine nitrogen sites can be expected during evaporative deposition of Al onto polybenzobisazole thin films in these devices.

The observed trends in the performance of MEH-PPV or PPV LEDs using the different polybenzobisazoles (Tables 1−3) cannot be explained or predicted solely from the HOMO/LUMO energy levels of Figure 5. The finding that PBZT and PBO are the best electron-transport materials among the series of 7 polybenzobisazoles can be understood in part from their combination of good barrier (0.4−0.6 eV) to hole injection from either PPV or MEH-PPV, i.e., good hole-blocking properties, and favorable energetic for electron transfer to the emissive polymer layer at the MEH-PPV(or PPV)−polybenzobisazole interface.[2b] However, this consideration of the energetic at the polymer−polymer interface cannot explain the better performance of PBZT compared to that of PBO. One likely factor to fully explain the trends among the polybenzobisazoles is electron *transport* in contrast to electron *injection*. Unfortunately, this factor cannot be fully evaluated here because only PBZT has a reported electron mobility (2×10^{-7} cm²/V).[19] It is likely that the mobility of electrons in PBZT is greater than that in PBO and the other polybenzobisazoles.

The present bilayer LEDs, especially ITO/MEH-PPV/ PBZT(or PBO)/Al and ITO/PPV/PBZT(or PBO)/Al, were repeatedly tested over a period of 9−10 months by storing them in air. Similar to the observed trends in the performance of the devices in terms of external quantum efficiency and luminance, LEDs using PBZT and PBO as the electron-transport layers were found to be most stable and durable in air. These LEDs showed smooth and reproducible current−voltage and luminance−voltage curves during the entire period of testing. About 5−10% decrease in performance was observed after 9−10 months of storage in air and the polymer films within the devices remained clear and homogeneous. In contrast, the performance of the single-layer MEH-PPV or PPV diode very rapidly decreased and failed after a day of fabrication and 2 cycles of testing. The substantially improved stability of MEH-PPV or PPV LEDs by using polybenzobisazoles as the electron-transport layers can be traced to the robust high-temperature resistance ($T_g > 400-500$ °C), excellent environmental, photochemical, and electrochemical stability of the polybenzobisazoles.[11−14]

The present results show that the polybenzobisazoles, especially PBZT and PBO, are better electron transport materials for arylene vinylene polymer LEDs in many respects as compared to reported oxadiazole- or triazole-containing molecules or polymers.[3,6,7] The turn-on (electric fields in the range of 2.3−7.5 $\times$ 10⁵ V/cm) and operating voltages, external quantum efficiencies, and even luminance of the present MEH-PPV and PPV LEDs are superior to prior ones using other electron-transport materials. The turn-on voltages of oxadiazole- or triazole-based devices are commonly as high as 18−32 V (electric fields in the range of 2−5 $\times$ 10⁶ V/cm) and the external quantum efficiencies were in the range of 0.2−1.0% for diodes tested in inert atmosphere.[3,6,7] Another important advantage of the present polybenzobisazole-containing LEDs is their relatively good

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ambient air stability and durability. The present polymer LEDs are also superior in performance and stability compared to devices using several other electron-transport polymers with reported external quantum efficiencies of 0.08−0.35%.[10,23,24]

Conclusions

We have observed substantially improved performance and stability in arylene vinylene polymer LEDs by using polybenzobisazoles as the electron-transport materials. The observed external quantum efficiencies of up to 2.5% for MEH-PPV-based LEDs and 0.24% for PPV-based LEDs by using polybenzobisazoles are significantly better than those of multilayer MEH-PPV or PPV LEDs incorporating a variety of current electron transport materials. The observed enhancement in LED performance (lower turn-on voltage, higher luminance, and higher EL efficiency) is due to the efficient electron-injection and -transport properties of the polybenzobisazoles. The performance of LEDs made with polybenzobisazoles was quite stable in repeated testing even after 9−10 months storage in air. These results demonstrate that robust, high-temperature resistant, polybenzobisazoles can be used as electron-transport and hole-blocking materials for constructing more efficient and stable polymer LEDs.

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