Light-Emitting Devices Based on a Poly(*p*-phenylenevinylene) Statistical Copolymer with Oligo(ethylene oxide) Side Groups

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ABSTRACT: We present the photo- and electroluminescence properties of the statistical copolymer, poly[2,5-bis(dimethyloctylsilyl)-1,4-phenylenevinylene)]-*co*-[2,5-bis(triethoxymethoxy)-1,4-phenylenevinylene)], BDMOS-*co*-BTEM-PPV, designed to combine the high efficiency of BDMOS-PPV, with the ion-coordinating ability of BTEM-PPV. We find that the photoluminescence efficiency is increased to about 17%, from 8.8% for BTEM-PPV. Single-layer light-emitting diodes with calcium (aluminum) cathodes exhibit luminances up to 1300 (10) cd/m^2 with an efficiency of ≈0.5 (0.01) cd/A. ITO/BDMOS-*co*-BTEM-PPV:LiTf (8 wt %)/Al devices display behavior typical of light-emitting electrochemical cells, LECs, with efficiencies up to 0.03 cd/A. These results show that this statistical copolymer approach is successful at improving the photoluminescence efficiency, while also granting sufficient ion coordination for LEC applications.

I. Introduction

The observation of electroluminescence in a poly(*p*-phenylenevinylene), PPV, based diode was first reported 10 years ago.[1] Ever since, the field has expanded, covering both the search for highly efficient luminescent polymers, across the full visible range,[2,3] and the optimization of device structures in order to maximize their efficiency. The first polymer-based light-emitting diode (LED) consisted of an ITO/PPV/Al structure, in which the formation yield of luminescent excitons (upon recombination of injected electrons and holes) was far from being optimized, because of both different electron/hole injection barriers and different mobilities of these carriers in the conjugated polymer. Furthermore, because of the hole/electron imbalance, the recombination zone was located closer to the cathode, where the quenching by the metal cathode is more effective than in the device “bulk”. Subsequently, the use of hole- and electron-transporting layers, to improve the yield of exciton formation in the luminescent polymer layer,[4] has been widely investigated.

A different device approach, leading to improved and balanced charge injection, was first reported by Pei et al.[5,6] These devices were named light-emitting electrochemical cells, LECs, in accordance with the author’s interpretation of the operation mechanism, based on electrochemical doping processes. LECs are devices using an electroluminescent polymer blended with an ion transporting polymer (such as poly(ethylene oxide), PEO) and a salt. It was shown that above a certain bias voltage, identified by Yu et al.[7] as E_g/e, with E_g the energy gap of the luminescent polymer, the presence of mobile ions essentially eliminates the charge injection barriers, leading to electrode/polymer ohmic contacts.

An alternative ionic space charge based model was proposed by deMello et al.,[8] with emphasis on the effect of ion accumulation at the interfaces between the polymer and the blocking electrodes on the width of the injection barriers. At present there is still an open debate about the operating mechanism, and the distribution of the electric field within the devices,[9] which is not addressed here.

In the LEC structure initially proposed, Pei et al. used PPV and a soluble PPV derivative, MEH-PPV. These polymers, however, do not possess ion-coordinating ability, and therefore they are not able to solvate the ions and allow a significant ion motion under an applied electric field. Hence, the ion-transporting poly(ethylene oxide), PEO, was blended with the conjugated polymers. However, in view of the different chemical composition of the two blended polymers, there is a strong tendency for phase separation. To overcome this problem, oligo(ethylene oxide) side groups have been covalently bonded to the conjugated polymer chain. This approach was initially reported by Pei and Yang[10] in a poly(fluorene)-based polymer and largely expanded to homo- or copolymers of the PPV type.[11−14]

A possible concern regarding previously reported PPV-type homopolymers with oligo(ethylene oxide) side groups, MTEM-PPV and BTEM-PPV, is that they exhibit relatively low photoluminescence, PL, efficiencies (0.6% and 8.8%, respectively[12]). As a result, a significant effort has been devoted to the investigation of copolymers combining monomers of highly luminescent polymers and monomers carrying ion-coordinating side groups of the ethylene oxide type.

In this paper we report the synthesis and luminescence properties of a statistical PPV-based copolymer, poly[2,5-bis(dimethyloctylsilyl)-1,4-phenylenevinylene)]-*co*-[2,5-bis(triethoxymethoxy)-1,4-phenylenevinylene)], BDMOS-*co*-BTEM-PPV, of which a preliminary report was previously presented.[15] In particular, we find that the PL efficiency is about 17%, which is in between the reported values of the corresponding homopolymers: i.e.,

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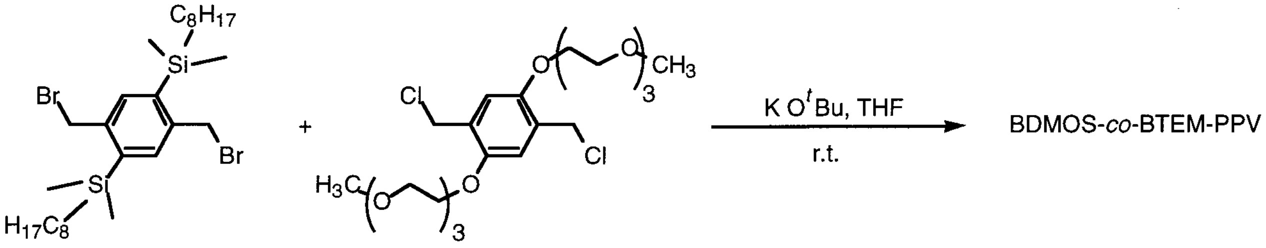
Scheme 1. Synthesis of the Statistical Copolymer Poly[2,5-bis(dimethyloctylsilyl)-1,4-phenylenevinylene)]-*co*-[2,5-bis(triethoxymethoxy)-1,4-phenylenevinylene)], BDMOS-*co*-BTEM-PPV



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>60% for BDMOS-PPV[16] and 8.8% for BTEM-PPV.[12] We also prepared LEDs and LECs and found that LEDs with calcium (aluminum) cathodes exhibit a maximum luminance of about 1300 (10) cd/m^2 with an efficiency of ≈0.5 (0.01) cd/A. Multilayer LEDs having a PPV layer between the ITO and the BDMOS-*co*-BTEM-PPV layer and a hole-blocking/electron-transporting layer of 2-(4-biphenylyl)-5-butylphenyl-1,3,4-oxadiazole between the copolymer layer and the aluminum cathode exhibit an EL efficiency of 0.78 cd/A, with a maximum luminance of about 100 cd/m^2. ITO/BDMOS-*co*-BTEM-PPV:LiTf (8 wt %)/Al devices display behavior typical of light-emitting electrochemical cells.

II. Experimental Section

(A) Polymer Synthesis and Characterization. The copolymer was prepared via the Gilch dehydrohalogenation route, using a 1:1 molar feed ratio of the corresponding monomers, 2,5-bis(dimethyloctylsilyl)-1,4-bis(bromomethyl)-benzene (**1**) and 2,5-bis(triethoxymethoxy)-1,4-bis(chloromethyl)benzene (**2**) (Scheme 1). The actual copolymer composition was estimated from ^{1}H NMR integration of acyclic OCH_3 and $SiCH_3$ peaks. It contains 31:69 molar ratio of BDMOS:BTEM units. The copolymer has a high molecular weight $M_n = 14\,000$, estimated from GPC in chloroform using polystyrene standards, with a polydispersity of 10.4.

The optical absorption and the photoluminescent studies were performed on thin films on Spectrosil B disks, deposited by spin coating from chloroform solutions. Absorption spectra were recorded with a Hewlett-Packard 8453 UV−vis spectrophotometer. The PL efficiency was determined as reported by deMello et al.,[17] using an integrating sphere, continuously purged with nitrogen to reduce the polymer photooxidation, upon excitation with the 496 nm line of an Ar ion laser. The PL spectra were recorded with a single-grating CCD UV-enhanced spectrograph (Oriel Instaspec IV).

The cyclic voltammetry study was performed in a film deposited over a platinum disk electrode, using a Pt wire as counter electrode, a Ag/AgCl reference, and 0.1 M of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile as electrolyte.

(B) Device Preparation and Characterization. Single-layer LEDs were prepared by spin coating the polymer solution in chloroform on top of ITO/glass substrates (previously treated with oxygen plasma for 10 min[18]). The structure was completed with thermal evaporation of the cathode material, aluminum or calcium (which was then protected with an overlayer of aluminum), at a base pressure of about 10^{-6} mbar, defining pixel areas of ≈4 mm^2. We prepared multilayer LEDs incorporating a PPV layer (30−35 nm thick), inserted between ITO and the BDMOS-*co*-BTEM-PPV emissive layer, and/or a hole-blocking/electron-transporting layer (HB/ETL) (≈35 nm thick), of 2-(4-biphenylyl)-5-butylphenyl-1,3,4-oxadiazole, PBD, inserted between BDMOS-*co*-BTEM-PPV and the aluminum cathode. PPV was prepared via the usual tetrahydrothiophenium-based precursor, by thermally induced conversion under vacuum for 10 h at 170 °C. The HB/ETL consisted of PBD dispersed in poly(methyl methacrylate) in a 3:1 ratio by weight, which was deposited by spin coating from an acetone solution. Polymer layer thickness was determined with a Dektak profilometer.

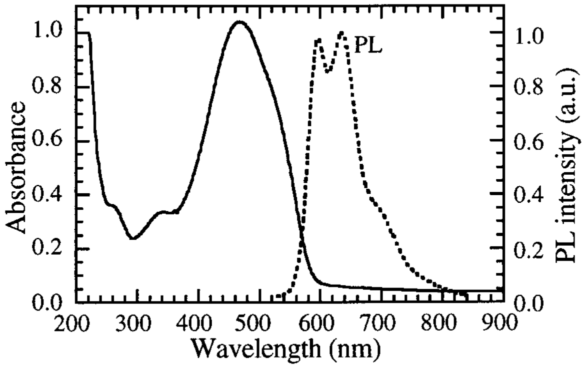

Figure 1. Optical absorbance and PL spectrum of a film (≈155 nm thick) of BDMOS-*co*-BTEM-PPV on Spectrosil B. PL was determined at an excitation wavelength of 496 nm.

The polymer solutions for LECs were prepared by adding lithium triflate, Li(CF_3SO_3) or LiTf, dissolved in acetonitrile to the BDMOS-*co*-BTEM-PPV solution in chloroform, to obtain a LiTf content of about 8 wt %. This solution was deposited by spin coating onto oxygen plasma treated ITO/glass substrates. The LEC structure was completed by thermally evaporating aluminum cathodes, obtaining pixel areas of 4 mm^2.

The devices were tested under vacuum (≈10^{-2} mbar). The internal EL quantum efficiency values were estimated according to Greenham et al.[19] The EL spectra were recorded with the CCD spectrograph used for PL studies.

III. Results

(A) Optical Properties. Figure 1 shows the absorption and the PL spectra recorded for a BDMOS-*co*-BTEM-PPV film, ≈155 nm thick. The optical absorption determined with the integrating sphere at 496 nm is 0.84, corresponding to an extinction coefficient of 5.4 × 10^4 cm^{-1}. The absorption onset occurs at about 590 nm (≈2.1 eV), which we take as the optical energy gap, $E_{g,opt}$. The absorption maximum, at 470 nm, is ≈10 nm blue-shifted in relation to the spectrum presented in a preliminary report.[15] This small difference is possibly related to the preparation conditions of the polymer solutions, namely the stirring time prior to filtration (through a 5 μm filter) as the polymer does not dissolve easily in chloroform, though this was found to be a slightly better solvent than THF. The PL efficiency for excitation at 496 nm is 17% typically, although, for a different preparation batch, a lower PL efficiency of 13% was obtained.

(B) Light-Emitting Diodes. Figure 2 compares the electrooptical characteristics of single- and double-layer

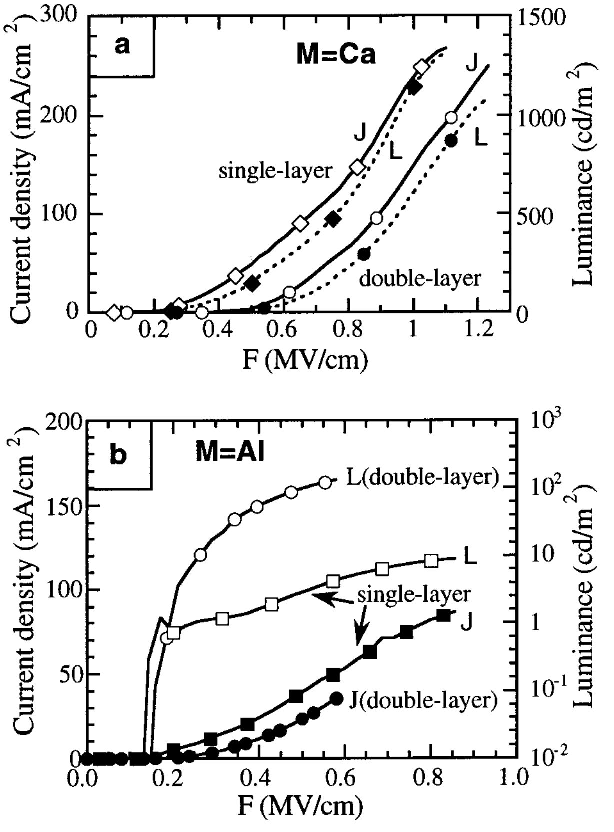

Figure 2. Electric field dependence of the current density (*J*) and of luminance (*L*) of single-layer ITO/copolymer/M and double-layer ITO/PPV/copolymer/M devices with (a) calcium and (b) aluminum cathodes. (The polymer film thickness is 270 nm for the Al-based LED and 230 nm for the Ca one.)

LEDs with aluminum or calcium cathodes. The current density and the luminance of the single-layer diodes, especially in the higher field range, are higher if Ca is used as cathode material instead of Al. A maximum luminance of about 1300 cd/m^2 is obtained for the Ca-based single-layer LEDs, with an EL efficiency of 0.5 cd/A, corresponding to an internal EL quantum efficiency of about 2%. When Al is used, the maximum luminance is only about 10 cd/m^2, with an EL efficiency on the order of 0.011 cd/A. The light-onset voltage of the Al-based single-layer device of Figure 2b is 5 V (luminance of 0.3 cd/m^2), reproducing the value previously reported[15] for a similar 250 nm thick device. Single-layer devices with calcium cathodes have smaller light-onset voltages ($\approx$3.5 V), as shown in Figure 2a. The incorporation of the PPV between the ITO and the active layer slightly decreases both current and luminance for a given electric field (calculated by dividing the voltage by the total device thickness). The EL efficiency is therefore not significantly altered. The effect of PPV is much more pronounced when Al is the cathode material. Though the current is similar or slightly reduced, as for the Ca-based LEDs, upon inclusion of the PPV layer, the maximum luminance increases by at least a factor of 10, i.e., from about 10 to 130 cd/m^2, and the EL efficiency at these maximum luminances increases from 0.011 to 0.38 cm/A. We note that the maximum EL efficiency of these double-layer devices is similar to that found for Ca-based single-layer LEDs (0.5 cd/A).

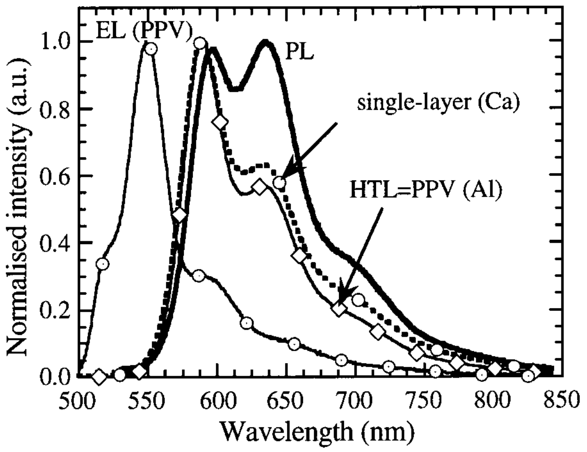

Figure 3. Comparison of the copolymer PL spectrum with the EL spectra of single-layer and of PPV containing double-layer devices. The PPV EL spectrum is also added for convenience of comparison.

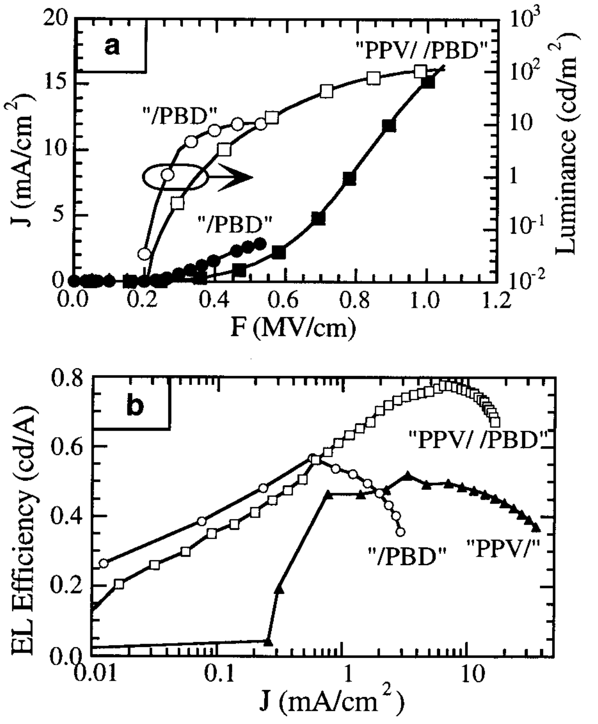

Figure 4. Characteristics of LEDs with either a PBD hole-blocking layer ("/PBD", circles) or PBD combined with a HTL of PPV ("PPV//PBD", squares) and with Al cathodes. (a) Current density (filled symbols) and luminance (open symbols) as a function of the average electric field. (b) EL efficiency as a function of the current density. The thickness of the copolymer layer is 155 nm. In (b) the EL efficiency of a double-layer LED with a HTL of PPV ("PPV/") is also shown for comparison.

EL spectra, shown in Figure 3, are similar to the emission spectrum previously reported for single-layer devices with Al cathodes.[15] Furthermore, Figure 3 shows there is no contribution from PPV to the emission of multilayer LEDs. Although excitons could also be formed within the PPV layer and then transfer to the emissive copolymer, we consider more likely that PPV only works as a transport layer.

The effect of the inclusion of the hole-blocking/electron-transporting PBD between the cathode and the active layer on current, luminance, and efficiency is summarized in Figure 4. A PBD layer was also used in conjunction with a PPV HTL in triple-layer diodes. The presence of the PBD drastically reduces the current density with respect to the single-layer devices, whereas

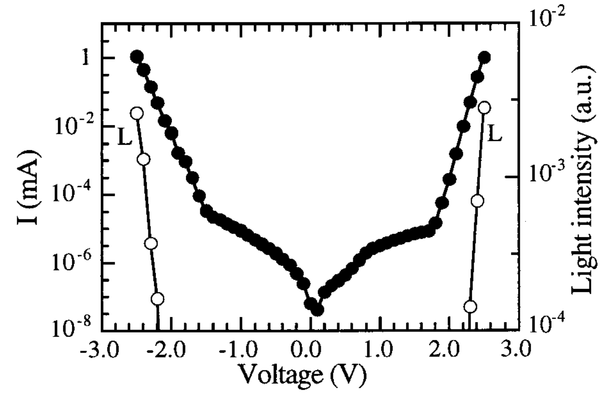

Figure 5. Current (filled circles) and light output (open circles) as a function of the applied voltage for an ITO/BDMOS-*co*-BTEM-PPV:LiTf(8 wt %)/Al device. The polymeric layer is 205 nm thick.

the maximum luminance is similar (≈10 cd/m^2), hence the increase of the EL efficiency. The highest EL efficiency for this multilayer configurations, 0.78 cd/A, is obtained when PPV and PBD are used simultaneously. This is also higher than the 0.5 cd/A for the two-layer ITO/PPV/copolymer/Al device, though the maximum luminance is slightly lower.

(C) Light-Emitting Electrochemical Cells. Figure 5 shows the electrooptical characteristics of a BDMOS-*co*-BTEM-PPV based LEC. Both current and light output exhibit antisymmetric and symmetric variation, respectively, with bias voltage. The light emission is first detected at +2.3 V, in forward bias, and at −2.2 V, under reverse bias. These voltages were obtained with a setup having a more sensitive light detection system than the one used to characterize the LECs reported in ref 15. As expected, they are lower than the turn-on voltage of 3 V previously reported. We note that, for the LECs reported in ref 15, the light emission is, in fact, first detected at about 2.5−2.6 V, reaching a luminance of 0.15 cd/m^2 at 3 V (which was taken as the turn-on voltage). Besides the different sensitivity of the two measurement setups, the higher thickness of the LECs reported in ref 15 (500 nm, compared to the 205 nm thickness of the LEC whose characteristics are shown in Figure 5), leading to longer response times, also contributes to a higher turn-on voltage, as a common voltage sweep of 0.1 V/5 s was used.

The results shown in Figure 5 refer to voltage sweeps in two different pixels of the same device. Although the characteristics are essentially symmetric during the first sweep, they tend to become more asymmetric after bias is reversed to start a new sweep. We attribute this behavior to the slow mass transport (ion displacement) which occurs under bias and which requires a stabilization time between voltage sweeps to allow initial conditions to be attained. The LECs maximum luminance is smaller (typically about 4 cd/m^2) than for the corresponding single-layer Al-based LEDs, whereas the maximum EL efficiency is higher (0.03 cd/A).

We have also characterized the transient response of these LECs. The current measured at time $t = 0$ for applied voltages below 1 V is mainly due to the ionic contribution. We found that this ionic current has a superlinear dependence on the applied voltage, which is consistent with the presence of ion aggregates.[8]

(D) Cyclovoltammetric Investigations. The reduction onset of BDMOS-*co*-BTEM-PPV occurs at −1.52 V and the oxidation onset occurs at +0.96 V, both vs Ag/AgCl reference electrode (−1.95 and +0.53 V, respectively, relative to ferrocene, Fc/Fc$^+$). As the energy level of ferrocene/ferrocenium (Fc/Fc$^+$) is estimated at 4.8 eV below the vacuum level,[20] we estimate the ionization potential (I_p) as 5.33 eV and the electron affinity (E_a) as 2.85 eV.

Table 1. Optical and Electrochemical Properties of BDMOS-*co*-BTEM-PPV and of the Corresponding Homopolymers

	BTEM-PPV	BDMOS-*co*-BTEM-PPV	BDMOS-PPV
PL:$S_1 \rightarrow S_0$/0−0 (high-energy peak) (nm)	598	597	525
PL efficiency (%)	8.8[12]	17	>60[16]
optical energy gap, E_g (eV)	2.12	2.10	2.50
reduction onset, E_{red} (V)	−1.94[a]	−1.95[b]	−2.28
oxidation onset, E_{ox} (V)	0.21[a]	0.53[b]	0.85
$E_{g,ec}$ (eV)[c]	2.15	2.48	3.13

[a] Measured against an Ag wire as a reference electrode. Values are corrected against ferrocene (Fc/Fc$^+$ 0.42 V). [b] Measured against an Ag/AgCl reference electrode. Values are corrected against ferrocene (Fc/Fc$^+$ 0.43 V). [c] $E_{g,ec}$ (eV) = E_{ox} (V) − E_{red} (V), electrochemical energy gap.

IV. Discussion

(A) Optical Properties and Electronic Structure. We note first that the highest energy peak of the PL spectrum of BDMOS-*co*-BTEM-PPV occurs at a wavelength similar to that for BTEM-PPV, suggesting that excitons decay predominantly from the lower E_g BTEM-PPV segments or BTEM-PPV-rich domains, which may be present owing to the statistical nature of BDMOS-*co*-BTEM-PPV. As the number of BTEM-PPV monomers is about twice the number of BDMOS−PPV monomers, we consider the first description more likely.

It is interesting that, in contrast to the strong similarity of the optical properties, the cyclic voltammetry, CV, data of BTEM-PPV and of the copolymer show significant differences (Table 1). In particular, we notice an increase of the copolymer ionization potential, IP (stabilization of the highest occupied molecular orbital, HOMO), with respect to BTEM-PPV, whereas the electron affinity is not significantly altered. The HOMO stabilization is expected upon replacement of the side-chain electron-donating oxy groups (BTEM-PPV) by silyl side groups. We note that (i) in previous CV studies[21] it was reported that the monosubstitution of silyl groups does not significantly influence the energy position of the frontier levels of PPV and (ii) calculations by Brédas and Heeger[22] showed that the oxy substitution destabilizes the PPV HOMO. (For example, in MEH-PPV it was confirmed by CV measurements[12] that the HOMO lies at −4.85 eV, being raised by 0.28 eV in relation to the HOMO of PPV.) Similarly, from the data in Table 1, we estimate that the HOMO of BTEM-PPV is raised by about 0.1 eV with respect to the HOMO of PPV.

It is maybe a little surprising that the presence of the silyl units does not decrease significantly the E_a of the copolymer with respect to BTEM-PPV, as would be expected in view of the reduced E_a of BDMOS-PPV. Quantum chemical calculations have shown that the presence of electron-donating methoxy groups substituted on the phenyl ring slightly decreases the E_a of PPV.[22]

The difference between the oxidation and the reduction onset voltages is usually designated as the electro-

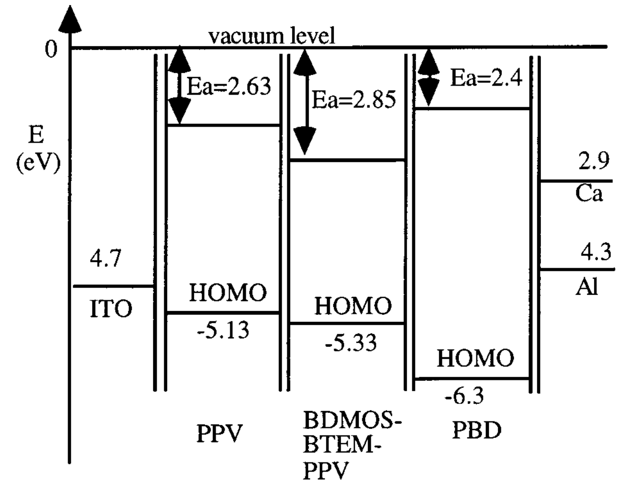

Figure 6. Energy position of the frontier levels of BDMOS-*co*-BTEM-PPV, PPV, and PBD, estimated from CV (HOMO energy and electron affinity, E_a).

chemical energy gap, $E_{g,ec}$. Its value for BDMOS-*co*-BTEM-PPV is 2.48 eV, slightly higher than the value of ≈2.1 eV calculated from the optical absorption onset (absorption edge). In the case of PPV, we also note that the optical energy gap, $E_{g,opt}$ (≈2.38 eV),[23] is smaller than the electrochemical value (2.55 eV, corresponding to an oxidation onset of +0.76 V and a reduction onset of −1.74 V, both vs Ag/AgCl).[24]

In Figure 6 we compare the energy position of the frontier levels of the several components used in the studied LEDs, including those of PPV[24] and PBD.[20] We consider the reported work function of 4.7 eV for oxygen plasma treated ITO.[18] Note that we consider that the energy level relevant for electron injection is the electron affinity, EA, as estimated from the reduction onset (CV data) rather than the energy level estimated as the HOMO energy plus the optical energy gap (and which is taken as the lowest unoccupied molecular orbital, LUMO, energy), as was also pointed out by Janietz et al.[25] We also consider that the ionization potential, IP, estimated from the onset of the oxidation potential, provides a good estimate of the HOMO position.

(B) Light-Emitting Diodes. As expected, we observe higher efficiency and current density for single-layer LEDs with calcium cathodes than for those with aluminum (as for PPV[23]), owing to easier electron injection from calcium (work function ≈2.8−2.9 eV vs 4.2−4.3 eV for Al).

All the multilayer LEDs with Al cathodes exhibit higher EL efficiencies than the single-layer device. The current density is not drastically affected by incorporation of the PPV layer, whereas it is significantly reduced if PBD is used between the copolymer layer and the Al cathode, as a result of hole blocking at the copolymer/PBD interface.

As shown schematically in Figure 6, as the HOMO of PPV is estimated to lie in between the ITO work function and the HOMO of the copolymer, the inclusion of the PPV layer does not increase the hole injection barrier from ITO to the copolymer. Instead, if the barrier heights alone are considered, the presence of PPV should facilitate the hole injection due to the creation of a graded barrier.

In addition, we expect holes to be less mobile within the statistical copolymer, on the basis of the increased energetic disorder, brought about by the statistical alternance of blocks with different conjugation lengths and different energetic position of the frontier levels. This should lead to hole accumulation close to the PPV/copolymer interface, which may, in turn, increase the electric field across the copolymer layer and facilitate electron injection from the Al cathode. We note that PPV has been reported to be a hole-type semiconductor, where the hole mobility (≈10^{-5} cm^2/(V s))[26] is much higher than the electron mobility.[27,28] We further note that, due to the preparation of PPV via the precursor route and possible surface oxidation, there may be also interfacial effects at the PPV/copolymer interface, not taken into account in Figure 6, and which could contribute to the observed current decrease upon inclusion of the PPV layer.

The effects of the PBD, clearly observed in the ITO/copolymer/PBD/Al devices, are consistent with the data in Figure 6. Namely, the decrease of the current density can be explained by the creation of a large hole-blocking barrier at the copolymer/PBD interface and increase of the electron injection barrier from Al. As a result, the light-onset field increases also. The increase of the EL efficiency results from reduction of the (hole) majority current, and possibly from hole accumulation at the copolymer/PBD interface, which helps electron injection from the cathode, thereby also improving the charge carriers balance. A third factor is the confinement of the recombination zone in a region closer to the copolymer/PBD interface, away from the quenching cathode.

When both PPV and PBD layers are present in a three-layer devices, the current density is much smaller than in the two-layer with PPV and similar to that of the double-layer with PBD, showing that it is PBD that controls the current. EL spectra of the multilayer LEDs show that the recombination still occurs within the copolymer layer.

The wavelength of the high-energy peak of the EL spectra, identical for the single- and double-layer devices, is closer to the corresponding peak of the PL spectra. As discussed above in relation to the PL spectra, we expect the electrically formed excitons to transfer to the BTEM-PPV domains, where they decay. The EL spectra of the multilayer devices incorporating PPV do not show any contribution of PPV to the emission, indicating that the recombination occurs within the BDMOS-*co*-BTEM-PPV layer, as expected, though, from the energy level diagram of Figure 6 alone, we cannot exclude the possibility that if excitons were formed within the PPV layer, they could be transferred to the copolymer.[29]

(C) Light-Emitting Electrochemical Cells. The results shown in Figure 5 clearly demonstrate that the oligo(ethylene oxide) side groups promote ion solvation and mobility. According to the predictions of the proposed operation models for LECs, but not always observed (as is the case for instance of LECs based on a ladder poly(*p*-phenylene)[14]), the current and light emission are nearly antisymmetric and symmetric, respectively, in relation to zero bias. The EL efficiencies are about 4 times the maximum value for the corresponding ITO/BDMOS-*co*-BTEM-PPV/Al diodes, as expected in view of the improved balance of injected charges. We note also that at higher voltages (above those shown in Figure 5) the luminance decreases, and this is accompanied by irreversible degradation of the devices.

The voltage at which luminance is first detected ranges from 2.0 to 2.3 V, in the forward bias direction, and from −2.1 to −2.2 V, under reverse bias conditions. These values compare well with the optical energy band gap of 2.10 eV determined from the absorption edge. They are also similar to the turn-on voltage of 2.0 V reported[30] for LECs based on the homopolymer BTEM-PPV.

The transient response studies are consistent with the existence of ion aggregates in films of the copolymer blended with LiTf. We have recently reported[13] on a similar behavior for LEC films based on an alternating copolymer also derived from BTEM-PPV (DB-*alt*-BTEM-PPV, DB = 2,3-dibutoxy-1,4-phenylenevinylene). We should mention, however, that the presence of the ion aggregates is not entirely attributed to the decrease of the ion-coordinating side groups on going from the homo- to copolymer, as its presence was also established[30] by infrared spectroscopy studies in BTEM-PPV + LiTf blends.

LECs prepared with copolymer + LiTf + PEO blends, in a weight ratio of about 10:1.3:2, failed to give symmetric current−voltage and luminance−voltage curves, at variance with the observations for LECs without PEO. Their EL efficiency in forward bias is about 0.49 cd/A, which is higher than the value of 0.03 cd/A for the LECs without PEO. Similarly to the results reported[13] for LECs based on DB-*alt*-BTEM-PPV, we attribute this increase of efficiency to a decrease of ion-induced exciton quenching, due to the decrease of ion concentration in close vicinity of the chains of the luminescent polymer. The blending of the copolymer with PEO may also lead to an increase of the PL efficiency, both because of reduction of aggregation effects, and therefore reduced tendency to formation of nonradiative interchain excited states, and also because of reduction of the exciton diffusion range and of the exciton probability of finding quenching centers before decay.

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References and Notes

(1) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.

(2) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 402.

(3) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; dos Santos, D. A.; Brédas, J.-L.; Lögdlund, M.; Salaneck, W. R. *Nature* **1999**, *397*, 121.

(4) Brown, A. R.; Bradley, D. D. C.; Burroughes, J. H.; Friend, R. H.; Greenham, N. C.; Burn, P. L.; Holmes, A. B.; Kraft, A. *Appl. Phys. Lett.* **1992**, *61*, 2793.

(5) Pei, Q.; Yu, G.; Zhang, C.; Yang, Y.; Heeger, A. J. *Science* **1995**, *269*, 1086.

(6) Pei, Q.; Yang, Y.; Yu, G.; Zhang, C.; Heeger, A. J. *J. Am. Chem. Soc.* **1996**, *118*, 3922.

(7) Yu, G.; Yang, Y.; Cao, Y.; Pei, Q.; Zhang, C.; Heeger, A. J. *Chem. Phys. Lett.* **1996**, *259*, 465.

(8) deMello, J. C.; Tessler, N.; Graham, S. C.; Friend, R. H. *Phys. Rev. B* **1998**, *57*, 12951.

(9) deMello, J. C.; Halls, J. J. M.; Graham, S. C.; Tessler, N.; Friend, R. H. *Phys. Rev. Lett.* **2000**, *85*, 421.

(10) Pei, Q.; Yang, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7416.

(11) Chuah, B. S.; Hwang, D. H.; Kim, S. T.; Moratti, S. C.; Holmes, A. B.; deMello, J. C.; Friend, R. H. *Synth. Met.* **1997**, *91*, 279.

(12) Hwang, D.-H.; Chuah, B. S.; Li, X.-C.; Kim, S. T.; Moratti, S. C.; Holmes, A. B.; deMello, J. C.; Friend, R. H. *Macromol. Symp.* **1997**, *125*, 111.

(13) Morgado, J.; Friend, R. H.; Cacialli, F.; Chuah, B. S.; Moratti, S. C.; Holmes, A. B. *J. Appl. Phys.* **1999**, *86*, 6392.

(14) Holzer, L.; Wenzl, F. P.; Sotgiu, R.; Gritsch, M.; Tasch, S.; Hutter, H.; Sampietro, M.; Leising, G. *Synth. Met.* **1999**, *102*, 1022.

(15) Rost, H.; Chuah, B. S.; Hwang, D. H.; Moratti, S. C.; Holmes, A. B.; Wilson, J.; Morgado, J.; Halls, J. J. M.; deMello, J. C.; Friend, R. H. *Synth. Met.* **1999**, *102*, 937.

(16) Chu, H. Y.; Hwang, D.-H.; Do, L.-M.; Chang, J.-H.; Shim, H.-K.; Holmes, A. B.; Zyung, T. *Synth. Met.* **1999**, *101*, 216.

(17) deMello, J. C.; Wittman, H. F.; Friend, R. H. *Adv. Mater.* **1997**, *9*, 230.

(18) Kim, J. S.; Granström, M.; Friend, R. H.; Johansson, N.; Salaneck, W. R.; Daik, R.; Feast, W. J.; Cacialli, F. *J. Appl. Phys.* **1998**, *84*, 6859.

(19) Greenham, N. C.; Friend, R. H.; Bradley, D. D. C. *Adv. Mater.* **1994**, *6*, 491.

(20) Pommerehne, J.; Vestweber, H.; Guss, W.; Mahrt, R. F.; Bässler, H.; Porsch, M.; Daub, J. *Adv. Mater.* **1995**, *7*, 5517.

(21) Kim, S. T.; Hwang, D.-H.; Li, X. C.; Grüner, J.; Friend, R. H.; Holmes, A. B.; Shim, H. K. *Adv. Mater.* **1996**, *8*, 979.

(22) Brédas, J.-L.; Heeger, A. J. *Chem. Phys. Lett.* **1994**, *217*, 507.

(23) Morgado, J.; Cacialli, F.; Grüner, J.; Greenham, N. C.; Friend, R. H. *J. Appl. Phys.* **1999**, *85*, 1784.

(24) Helbig, M.; Horhold, H. *Makromol. Chem.* **1993**, *194*, 1607.

(25) Janietz, S.; Bradley, D. D. C.; Grell, M.; Giebeler, C.; Inbasekaran, M.; Woo, E. P. *Appl. Phys. Lett.* **1998**, *73*, 2453.

(26) Lebedev, E.; Dittrich, Th.; Petrova-Koch, V.; Karg, S.; Brütting, W. *Appl. Phys. Lett.* **1997**, *71*, 2686.

(27) Wu, P.; Jikei, M.; Kakimoto, M.; Imai, Y. *Mol. Cryst. Liq. Cryst.* **1995**, *267*, 441.

(28) Blom, P. W. M.; de Jong, M. J. M.; Vleggaar, J. J. M. *Appl. Phys. Lett.* **1996**, *68*, 3308.

(29) Halls, J. J. M.; Cornil, J.; dos Santos, D. A.; Silbey, R.; Hwang, D.-H.; Holmes; A. B.; Brédas, J. L.; Friend, R. H. *Phys. Rev. B* **1999**, *60*, 5721.

(30) Holzer, L.; Winkler, B.; Wenzl, F. P.; Tasch, S.; Dai, L.; Mau, A. W. H.; Leising, G. *Synth. Met.* **1999**, *100*, 71.

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