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6. AUTHOR(S) Xuejun Zhang, Ashok S. Shetty, and Samson A. Jenekhe				
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Center for Photoinduced Charge Transfer  
University of Rochester, New York 14627

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# Efficient light-emitting diodes from blends of conjugated polymers

Xuejun Zhang, Ashok S. Shetty, and Samson A. Jenekhe

Departments of Chemical Engineering and Chemistry and Center for Photoinduced Charge Transfer, University of Rochester, Rochester, New York 14627-0166

## ABSTRACT

Electroluminescent devices from binary blends of conjugated polyquinolines are fabricated and used to systematically investigate the mechanisms of efficient electroluminescence (EL) in multicomponent conjugated polymer systems. The roles of energy transfer, excited state complex formation, charge transport and trapping, miscibility and phase separation, and spatial confinement on EL efficiency can be directly probed by a judicious choice of binary blend components. Large enhancement of EL efficiency and device brightness was observed in some conjugated polymer blend systems compared to the component homopolymers. For example, binary blends of poly(2,2'-(2,5-thienylene)-6,6'-bis(4-phenylquinoline)) and poly(2,2'-(biphenylene)-6,6'-(4-phenylquinoline)) are found to exhibit EL quantum efficiency of up to a factor of 30 enhancement at 200 cd/m<sup>2</sup> luminance levels compared to the components. EL enhancement in this and other polymer blend systems is shown by electric field-modulated photoluminescence spectroscopy and other experiments to be due to improved radiative electron-hole recombination efficiency facilitated by spatial confinement of excitons in the blends.

**Keywords:** light emitting diodes; polymer blends; electroluminescence mechanisms; polyquinolines; electroluminescence enhancement.

## INTRODUCTION

Conjugated polymers are now well established to be promising electroluminescent materials for developing high performance light-emitting diodes.<sup>1-3</sup> Recently, blends of two or more conjugated polymers have been shown to exhibit novel electronic, optical, and optoelectronic properties not found in the components, including efficient energy transfer and enhanced luminescence,<sup>4</sup> photoinduced electron transfer,<sup>5</sup> bipolar charge transport,<sup>6</sup> enhanced electroluminescence,<sup>7-9</sup> improved photoconductivity,<sup>10</sup> and enhanced nonlinear optical<sup>11</sup> properties. Also, very recently, our laboratory has demonstrated that large arrays of organic quantum-well structures, such as quantum wires and quantum boxes can be constructed by self-organization of blends of a block conjugated copolymer with a parent conjugated homopolymer.<sup>12</sup> Blends of conjugated polymers are thus promising optoelectronic materials for exploring device applications, such as light-emitting diodes and photodetectors.

Studies of light-emitting diodes (LEDs) fabricated from blends of conjugated polymers have revealed novel effects not seen in LEDs from the pure component homopolymers.<sup>7-9,13-14</sup> Voltage-tunable electroluminescence (EL) color was observed in phase-separated blends of several polythiophene derivatives.<sup>13</sup> Excitation energy transfer, between the blend components, and phase separation on the 50-200 nm scale, which is comparable or larger than the emitter thickness in the devices, were suggested to be the origin of the multicolor LED emission.<sup>13</sup> White light EL emission has been observed from ternary blends of poly(3-(4-octylphenyl)-2,2'-bithiophene), poly(3-methyl-4-octylthiophene), and poly(3-cyclohexyl thiophene).<sup>14</sup> Dramatic enhancement of EL quantum efficiency and the brightness of LEDs fabricated from binary polymer blends, compared to the component polymers, has been reported by three laboratories: blends of poly(3-hexylthiophene) and poly(2-methoxy-5-(2'-ethylhexoxy)-1,4-phenylenevinylene) (MEH-PPV);<sup>8</sup> blends of MEH-PPV and poly(1,3-propane-dioxy-1,4-phenylene-1,2-ethylene(2,5-bis(trimethylsilyl)-1,4-phenylene)-1,2-ethenylene-1,4-phenylene);<sup>9</sup> and blends of two polyquinolines which are described below. Although excitation energy transfer was thought to be the origin of the observed EL enhancement in

both MEH-PPV blend systems,<sup>8,9</sup> other possible photophysical and physical mechanisms of EL enhancement in polymer blends cannot be ruled out. For example, depending on the electronic structures of the components of a polymer blend, other photophysical processes such as excited state complex formation<sup>15</sup> and photoinduced electron transfer<sup>5</sup> are possible. The possible different roles of *spatial confinement* and *exciton transfer* must be delineated in polymer blends; the former effect will be very sensitive to the composition whereas the latter effect will be independent of the blend composition.

In this paper, we report the electroluminescence of several binary blends of conjugated rigid-rod polyquinolines used as model systems to explore the roles of electronic structure, exciton transfer (excitation energy transfer), spatial confinement of excitons, and morphology on EL efficiency and features of LEDs based on multicomponent polymer systems. Conjugated polyquinolines are a class of polymers which exhibit good processibility, excellent thermal stability, high mechanical strength,<sup>16,17</sup> and interesting electronic,<sup>17(b)</sup> photoconductive,<sup>18</sup> and nonlinear optical<sup>19</sup> properties. We have previously reported that conjugated polyquinolines are good electroluminescent materials<sup>20</sup> and showed that they exhibit good electron-transport (n-type) properties as revealed by electrochemistry<sup>21</sup> and in devices.<sup>20</sup> Polyquinolines used in this study include: poly(2,6-(4-(p-tert-butyl)phenyl)quinoline) (Bu-PQ), poly(2,2'-(2,5-thienylene)-6,6'-bis(4-phenylquinoline)) (PTPQ), poly(2,2'-(biphenylene)-6,6'-(4-phenylquinoline)) (PBPQ), poly(2,2'-(p-phenyl)-6,6'-bis(4-phenylquinoline)) (PPPQ), and poly(2,2'-(p-phenyl)-6,6'-bis(4-(p-tert-butyl)phenyl)quinoline) (Bu-PPQ). Four binary blend systems were investigated: PTPQ:PBPQ, Bu-PQ:PBPQ, Bu-PQ:Bu-PPQ, and PPPQ:Bu-PPQ. The chemical structures of the conjugated polyquinolines investigated are shown in Figure 1. Because all the polyquinolines and their binary blends are good electron transport (n-type) and emissive materials, their electroluminescence was investigated in a bilayer device structure including a hole transport layer consisting of 1,1-bis(di-4-tolylaminophenyl)cyclohexane (TAPC) dispersed in polystyrene. The structure of TAPC is also shown in Figure 1.

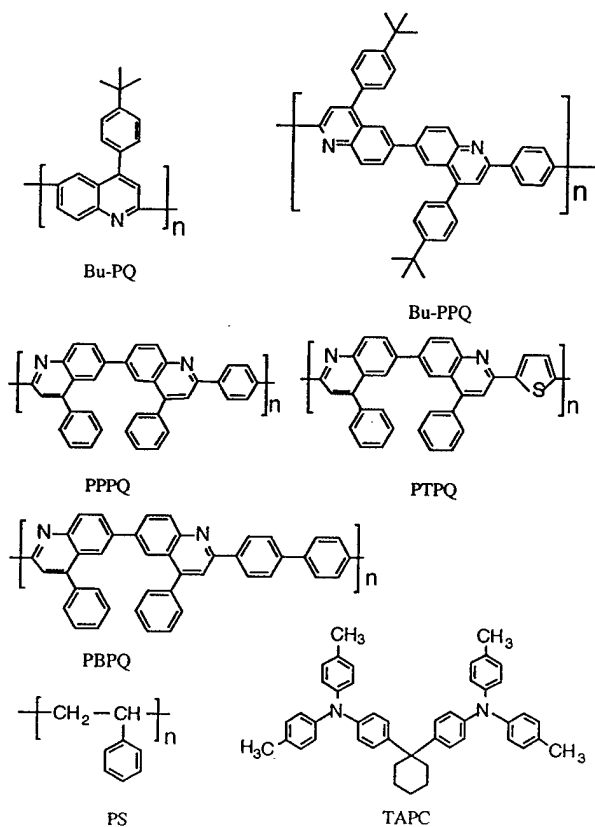


Figure 1. Molecular structures of materials used in this study.

## EXPERIMENTAL SECTION

**Materials.** All the polyquinolines used in this study were synthesized in our laboratory. The synthesis and detailed characterizations were reported previously.<sup>17(b),20(b)</sup> Intrinsic viscosities of these polymers are in the range of 3 to 12 dL/g in 0.1 mol% di-*m*-cresol-phosphate/*m*-cresol at 25 °C or in methanesulfonic acid at 30 °C, indicating that they are high molecular weight materials.

**Preparation of blends and thin films.** Binary blends of the two conjugate polyquinolines were prepared by dissolving binary mixtures in formic acid solvent. The resulting solutions (0.3–0.4 wt.% total polymers in the solvent) were homogeneous. Concentrations of blends in this paper refer to weight. Optical quality thin films of homopolymers or polymer blends were obtained by spin-coating from formic acid solutions. Films for optical absorption and photoluminescence measurements were spin-coated onto silica substrates. All the films were dried overnight at 60 °C in vacuum. Polymer blend films (30–60 nm) were homogeneous and showed excellent optical transparency. No visible phase-separation was observed. Additional steps in the preparation of devices will be described below.

**Optical absorption and photoluminescence spectroscopy.** Optical absorption spectra were obtained by using a Lambda-9 UV/Visible/Near-IR spectrophotometer (Perkin-Elmer). Steady-state photoluminescence studies were carried out by using a Spex Fluorog-2 Spectrofluorimeter. The films were positioned such that the emitted light was detected at 22.5° from the incident beam.

**Electrochemistry.** Electrochemical (redox) properties of the newly synthesized polyquinolines (Bu-PQ and Bu-PPQ) were investigated by using cyclic voltammetry (CV). Platinum (Pt) wire electrodes were used as both counter and working electrodes, and Ag/Ag<sup>+</sup> electrode was used as the reference. Polymers were coated onto the working electrode by dipping the Pt wire electrodes into viscous polymer solutions. CV measurements were done in an electrolyte solution of 0.1M tetrabutylammonium tetrafluorophosphate in acetonitrile. The detailed experimental procedures were the same as previously reported.<sup>21</sup>

**Device fabrication and characterization.** Electroluminescent devices were prepared and investigated as sandwich structures between aluminum and indium-tin oxide (ITO) electrodes (Figure 2). 1,1-Bis(di-4-tolylaminophenyl)cyclohexane (TAPC) dispersed in polystyrene (PS) was used as the hole-transport layer.<sup>22</sup> The TAPC:PS (50 wt%) thin films (50 nm) were deposited onto ITO coated glass substrates by spin coating from dichloromethane solutions. Thin films (30–60 nm) of the conjugated polyquinolines or blends were spin coated from their formic acid solutions onto the TAPC:PS layer and dried at 60 °C in vacuum overnight. The film thicknesses were measured by an Alpha-step profilometer (Tencor Northern) with an accuracy of ±1 nm and confirmed by an optical absorption coefficient technique. Finally, 100–130 nm aluminum electrodes were vacuum ( $5 \times 10^{-6}$  torr) evaporated onto the resulting bilayers. The area of each EL device was 0.2 cm<sup>2</sup>. Electroluminescence spectra were obtained by using a Spex Fluorog-2 spectrofluorimeter. Current-voltage-luminance characteristic were recorded simultaneously by hooking up an HP4155A semiconductor parameter analyzer together with a Grasby S370 optometer equipped with a luminance sensor head. The EL quantum efficiencies of the diodes were estimated by using procedures similar to those previously reported.<sup>23</sup> All the fabrication and measurements were done under ambient laboratory conditions.

**Electric field-modulated photoluminescence spectroscopy.** Electric field modulated photoluminescence (PL) measurements were performed on the same electroluminescent devices described above by photoexciting a sample and obtaining PL emission spectra under applied bias voltages. Both forward (positive to ITO) and reverse bias voltages gave identical spectra as long as there is no significant current flow. The device was positioned such that the emitted light was detected from the ITO side at 22.5 ° relative to the incident beam. All the experimental conditions are the same as in steady state PL measurements for thin films on silica substrates.

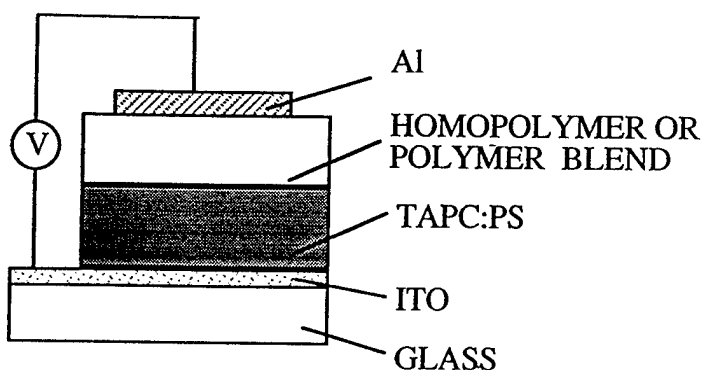


Figure 2. Schematic of the bilayer electroluminescent device.

## RESULTS AND DISCUSSION

**Optical absorption and photoluminescence.** Figure 3(a) shows the absorption spectra of thin films of the polyquinolines (Bu-PQ, Bu-PPQ, PPPQ, PBPQ, and PTPQ) on silica substrates. The absorption maxima and the optical absorption bandgaps determined from the absorption edges are listed in Table 1. Bu-PPQ, PPPQ, and PBPQ have very close absorption spectra (absorption peaks and bandgaps) due to their structural similarities. However, Bu-PQ and PTPQ show gradual bathochromic shifts in both the absorption peaks and bandgaps. For example, Bu-PPQ and PPPQ have absorption peaks at 399 and 400 nm, respectively, and the same bandgap of 2.78 eV. PBPQ has an absorption peak at 405 nm and a bandgap of 2.81 eV. Bu-PQ has an absorption peak at 412 nm and a bandgap of 2.65 eV. PTPQ has an absorption peak at 471 nm and a bandgap of 2.49 eV. As we previously reported for PTPQ:PBPQ blend system,<sup>7</sup> all the absorption spectra of binary blends are simple superpositions of those of the component polymers. New absorption features were not observed in the range of 200-2,800 nm, suggesting that the two component polymers of the blend have little or no interactions in their electronic ground states.

Table 1. Optical absorption maxima, PL maxima, bandgaps, and redox potentials of polyquinolines.

Polymer	$\lambda_{\max}(\text{ABS})$ (nm)	$\lambda_{\max}(\text{PL})$ (nm)	$E_g^{\text{opt}}$ (eV)	$E_{\text{red}}$ (V) <sup>a</sup>	$E_{\text{ox}}$ (V) <sup>b</sup>
Bu-PQ	412	574	2.65	-1.86	0.79
Bu-PPQ	399	540	2.78	-1.58	1.20
PPPQ	400	571	2.78	-1.90	0.88
PBPQ	405	571	2.81	-1.98	0.83
PTPQ	471	622	2.49	-1.84	0.65

a.  $E_{\text{red}}$  values are onset potentials versus SCE. The data for PPPQ, PBPQ and PTPQ are from ref. 18.

b.  $E_{\text{ox}}$  was calculated from  $E_{\text{ox}} = E_g^{\text{opt}} - |E_{\text{red}}|$ .

The photoluminescence (PL) spectra of the five conjugated polyquinolines are shown in Figure 3(b). The PL emission peaks of the polymers are also listed in Table 1. The PL emission colors of these polyquinolines are green-yellow (Bu-PPQ), orange (Bu-PQ, PPPQ, and PBPQ), and red (PTPQ). These polymers showed structureless emission spectra with large Stokes shift from 139 nm for Bu-PPQ to 171 nm for PPPQ. These characteristics are typical of excimer emissions from rigid-rod conjugated polymers.<sup>15</sup> On

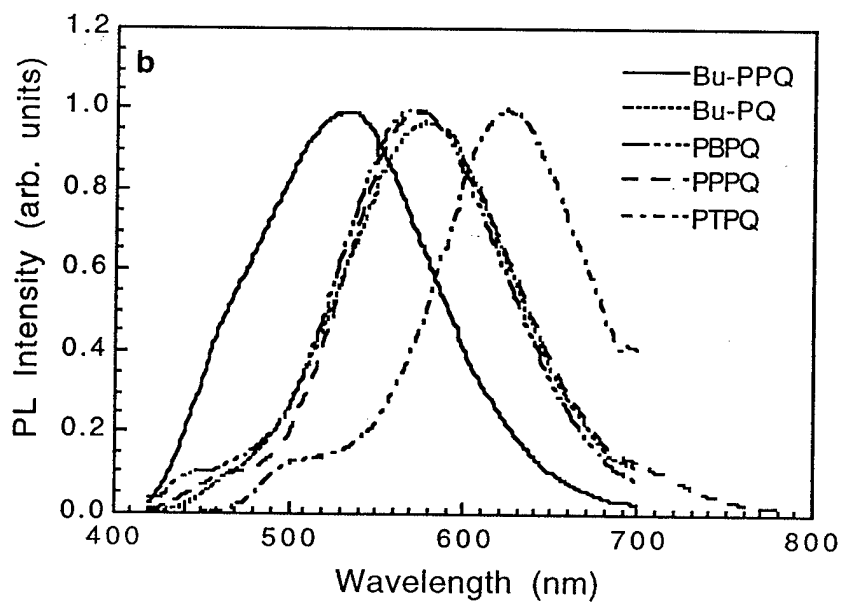
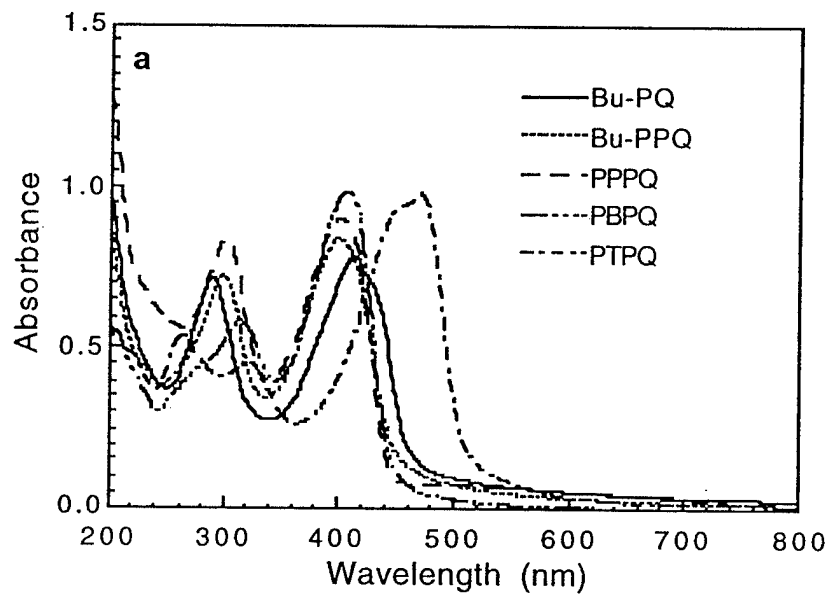


Figure 3. Thin film optical absorption (a) and photoluminescence (b) spectra of polyquinolines.

the other hand, when compared to the optical absorption spectra, it can be seen that in the four blend systems (PTPQ:PBPQ, Bu-PQ:PBPQ, Bu-PQ:Bu-PPQ, and Bu-PPQ:PPPQ) there is no significant spectral overlap between optical absorption and photoluminescence spectra of the two components. Therefore, radiative energy transfer as well as nonradiative energy transfer (exciton transfer) in these blends will be negligible.<sup>4</sup> However, other photophysical processes, such as electron transfer and exciplex formation can not be ruled out.

PL spectra of blends were found to be dependent on composition of the blends. Figure 4(a) shows representative PL spectra for Bu-PQ:Bu-PPQ blend system. PL emission spectra of Bu-PQ:Bu-PPQ blends (0.1-5% Bu-PQ) are between those of Bu-PQ and Bu-PPQ. For example, the emission peak of the 5% blend is 558 nm, whereas the emission peaks of Bu-PQ and Bu-PPQ are 574 and 540 nm, respectively. As discussed in detail elsewhere,<sup>7</sup> the photoluminescence of conjugated polymer blends, such as mixtures of polyquinolines, is a complicated function of composition and bimolecular photophysical processes. Since excimer emission is known to be dominant in thin films of the conjugated rigid-rod homopolymers,<sup>15</sup> both single chain ( $A^*$ ,  $B^*$ ) and excimer [ $(AA)^*$ ,  $(BB)^*$ ] emission can be anticipated in binary blends. In addition, excitation energy transfer [ $A^* + B \rightarrow A + B^*$ ], exciplex formation [ $A^* + B \rightarrow (A^{\delta+}-B^{\delta-})^*$ ], or electron transfer [ $A^* + B \rightarrow A^{\cdot+} + B^{\cdot-}$ ] can also occur in blends. Thus, in the electroluminescence of binary blends, the emissive excited states  $A^*$ ,  $B^*$ ,  $(AA)^*$ ,  $(BB)^*$ , and  $(A^{\delta+}-B^{\delta-})^*$  can be formed by electron-hole recombination followed by additional photophysical processes. Charge transport and trapping which may influence EL but not photoluminescence can also be significantly modified in binary blends, compared to homopolymers, as a consequence of bimolecular excited state interactions such as electron transfer or exciplex formation.

**Electroluminescence.** The EL spectra of homopolymers and blends of the polyquinolines were found to be similar to the corresponding PL spectra at low bias voltages. At higher forward bias voltages, EL spectra of blends were significantly blue shifted from the corresponding PL spectra. Representative EL spectra of Bu-PQ:Bu-PPQ blend system are shown in Figure 4 and those of the Bu-PQ:PBPQ and PPPQ:Bu-PPQ blend systems are shown in Figure 5. The main feature of the blend EL spectra is that at low concentrations (< 10 wt%) of the dispersed component, the blend EL emission spectra are spectrally similar to the matrix EL spectra. Thus, the 0.1-5.0 wt% blends shown in Figures 4 and 5 have EL spectra that are almost identical to the EL spectra of Bu-PPQ and PBPQ which are the matrix polymers in the four blend systems. These blend EL spectra results are to be contrasted with those expected in simple energy transfer binary blend systems where enhanced emission from the dispersed, minority, and lower-energy component ( $B^*$ ) is observed at the expense of the higher-energy matrix ( $A^*$ ).<sup>4</sup>

The turn-on voltage characteristics of the blend LEDs, as determined by either current-voltage (I-V) or luminance-voltage (L-V) curves, were in the ranges of 6-7.5 V, 8-9 V, 9-10 V, and 8-9 V for the PTPQ:PBPQ, Bu-PQ:PBPQ, Bu-PQ:Bu-PPQ, and PPPQ:Bu-PPQ blend systems, respectively. These turn-on voltages are essentially identical to those of the corresponding homopolymer devices. Figure 6 shows the current-electric field and luminance-electric field characteristics of the Bu-PQ:PBPQ blend system. All the LEDs turned on around  $10^6$  V/cm. Figure 6(a) shows that the current-electric field characteristics of Bu-PQ:PBPQ blends tend to be close to that of the pure Bu-PQ and very different from that of PBPQ which is matrix polymer in this blend system. This may imply that charge transport, trapping, and recombination processes in Bu-PQ:PBPQ blends are greatly different from those in the pure PBPQ. On the other hand, as shown in Figure 6(b), the luminance of the blends was enhanced by a factor of 2 to 4 times compared to the pure polymers. It can be seen that the 1% blend has a luminance of about 200  $\text{cd/m}^2$ , whereas the 0.5% and 1% blends show luminance of about 170  $\text{cd/m}^2$ . The LEDs made from the components, Bu-PQ and PBPQ, had luminance levels of  $\sim 100$  and  $\sim 60$   $\text{cd/m}^2$ , respectively.

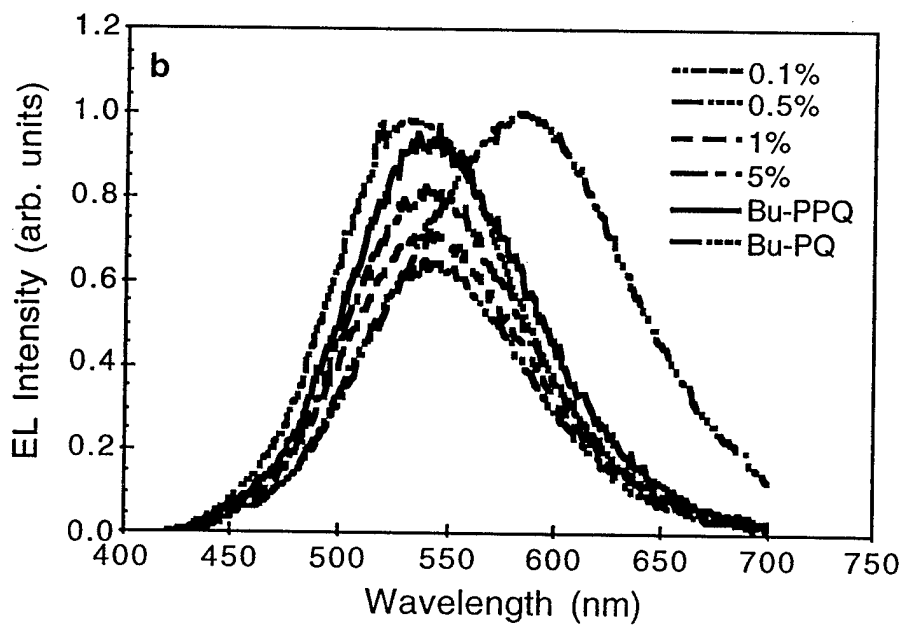
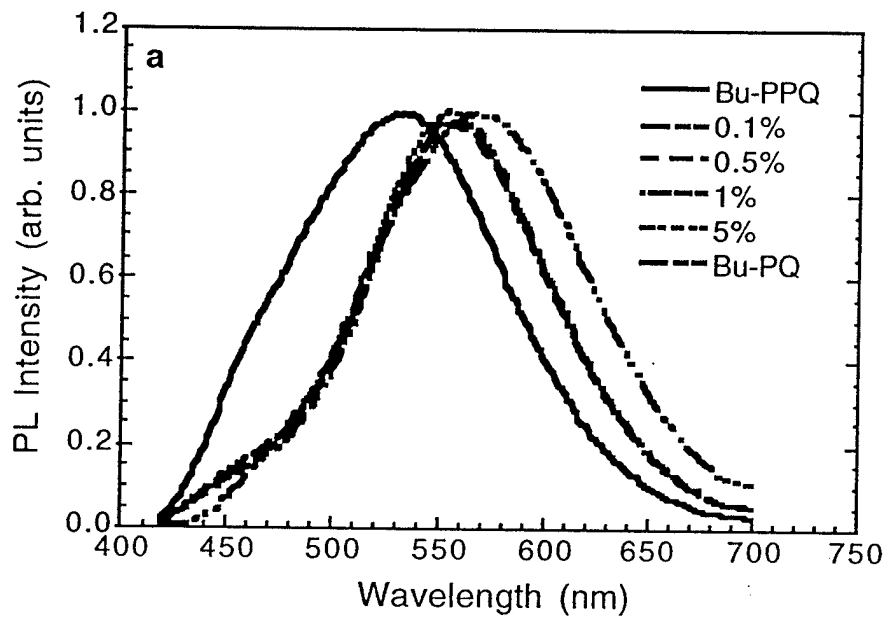


Figure 4. Photoluminescence (a) and electroluminescence (b) spectra of Bu-PQ:Bu-PPQ blends.

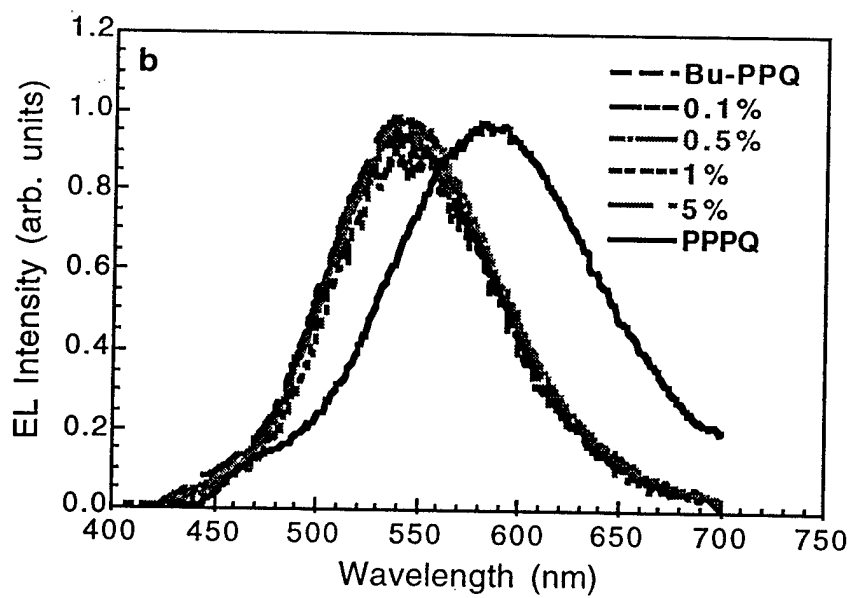
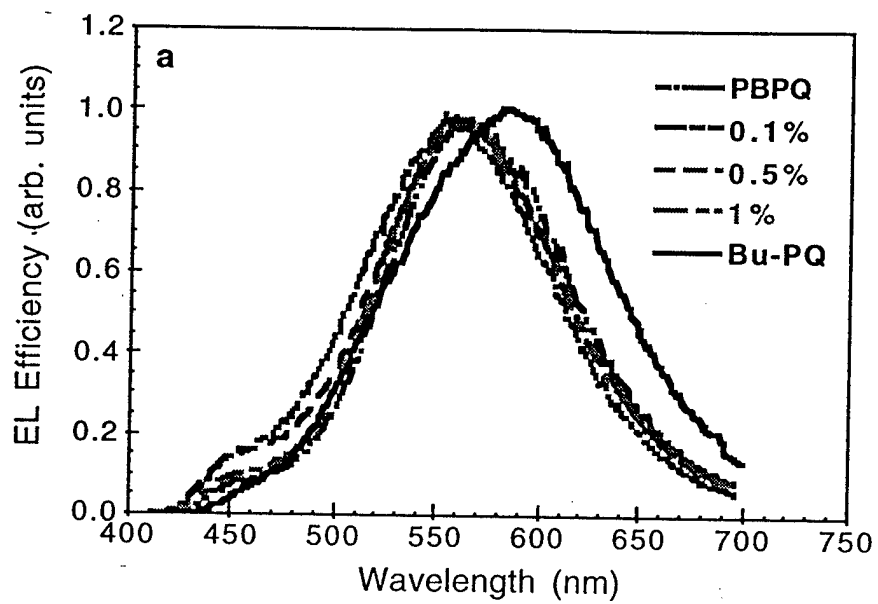


Figure 5. Electroluminescence spectra of Bu-PQ:PBPQ (a) and PPPQ:Bu-PPQ (b) blend systems.

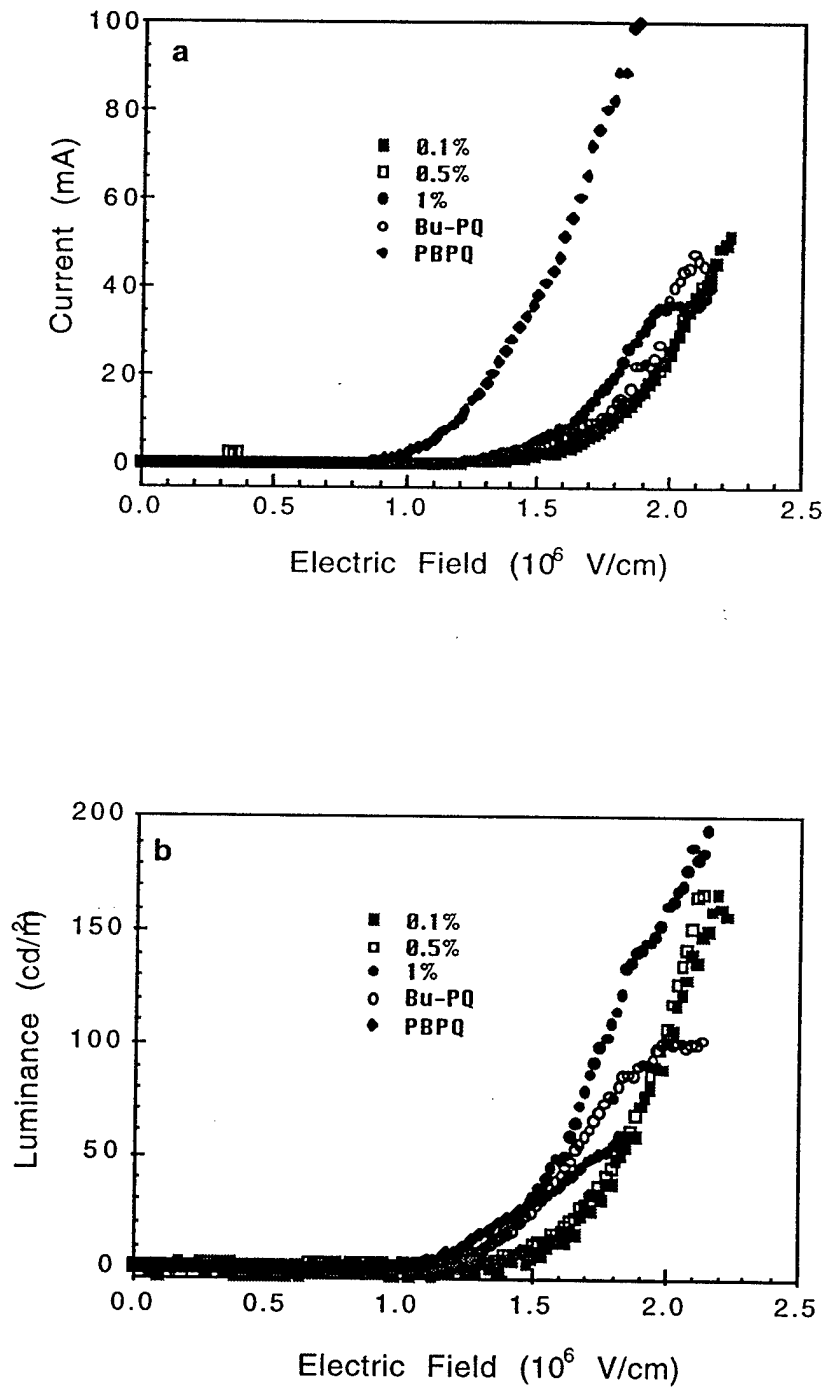


Figure 6. Current-electric field (a) and luminance-electric field (b) characteristics of Bu-PQ:PBPQ blend system.

EL quantum efficiency (photons/electron) of LEDs made from binary blends, compared to devices from the component homopolymers, was dramatically enhanced in PTPQ:PBPQ and Bu-PQ:PBPQ blends but not enhanced at all in the other two blend systems (Bu-PQ:Bu-PPQ and PPPQ:Bu-PPQ). For example, the main results for the PTPQ:PBPQ blend system listed in Table 2 show that whereas the EL quantum efficiency is 0.004 and 0.03%, respectively, for PTPQ and PBPQ homopolymers, the 0.1% blend has an efficiency as high as 0.11%. Such a large EL efficiency enhancement was only observed in blends with 10% PTPQ or less. In the case of PTPQ:PBPQ blends, the observed enhancement of EL quantum efficiency and luminance were factors of 4–30 compared to the two components. Similar EL enhancements in Bu-PQ:PBPQ blend LEDs were about factors of 2–4 whereas no enhancement was observed in the other two blends (Bu-PQ:Bu-PPQ and PPPQ:Bu-PPQ).

Table 2. EL efficiencies of PTPQ:PBPQ blends.

wt%, PTPQ	0	0.1	1	5	10	20	30	50	100
EL Efficiencies, %	0.030	0.110	0.070	0.080	0.010	0.016	0.009	0.008	0.004

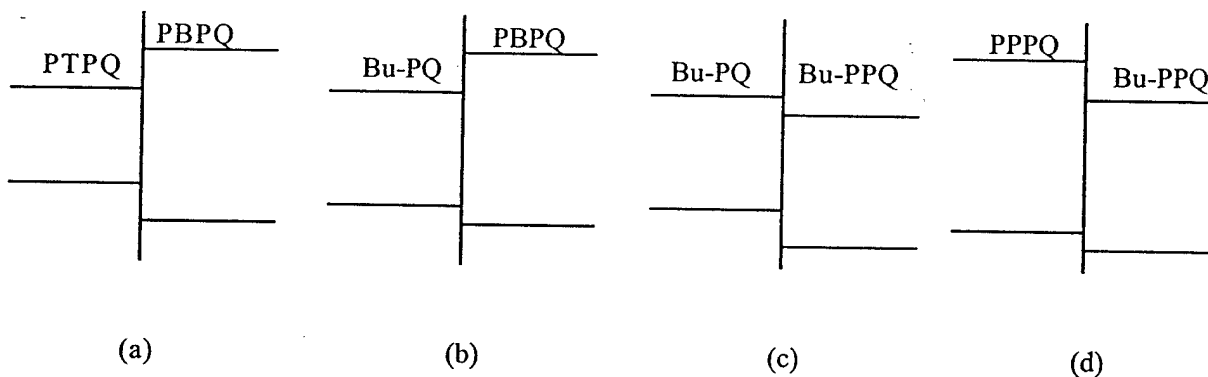


Figure 7. Schematic of HOMO-LUMO levels of four polyquinoline blend systems.

**Origin of EL enhancement in conjugated polymer blends.** Previous observations of enhancement of electroluminescence in polymer blends have been attributed to improved charge carrier injection, improved charge transport, and Förster-type energy transfer from the higher excitation energy component to one with lower excitation energy.<sup>8,9</sup> Our prior detailed study of Förster-type (dipole-dipole) energy transfer in binary conjugated polymer blends showed that the luminescence efficiency of a “guest chromophore” or minor component can be dramatically enhanced while the luminescence of the “host chromophore” or matrix polymer was quenched.<sup>4</sup> EL enhancement in the blends of conjugated polyquinolines reported here, cannot be satisfactorily explained by these prior suggestions. In fact, we can clearly rule out improved carrier injection and charge transport as possible factors in the observed EL enhancement. This is because of the similarity of the I-V, L-V, EL turn-on voltage, and EL spectra of the blends to those of the host or majority component in the polymer blends discussed above. We propose that EL enhancement in binary blends of the polyquinolines arise primarily from the spatial confinement of excitons in the dispersed (minority) component. Although there is negligible overlap between the emission spectra of the higher-energy components (A) and the absorption spectra of the lower-energy components (B) of the four AB blends, thus ruling out any significant radiative or nonradiative (Förster type) dipole-dipole energy transfer [ $A^* + B \rightarrow A + B^*$ ], Dexter-type energy transfer via electron exchange is feasible in two of the blend systems (PTPQ : PBPQ, Bu-PQ:PBPQ) as shown in the energy level diagrams of Figure 7.

Dexter-type exciton transfer from A to the lower-energy component B (i.e. PTPQ, Bu-PQ) is feasible in PTPQ:PB PQ and Bu-PQ:PB PQ blends in which EL enhancement was observed whereas it is not feasible in the remaining two blend systems (Figure 7). However, exciton transfer is not enough to explain the observed composition-dependent EL quantum efficiency and luminance. Spatial confinement of excitons achieved with dilute concentrations ( $< 10\%$ ) of the "guest" component B ensures improved radiative recombination and exciton stability in the two blend systems in which EL enhancement was observed.

Spatial confinement induced exciton stability was explored in the binary blends by applying electric field-modulated photoluminescence (EFM-PL) spectroscopy. Electric field-induced photoluminescence quenching in pure conjugated polymers which is caused by the exciton dissociation, is well known.<sup>12(b),24</sup> Also, the exciton stability due to spatial confinement in conjugated polymer quantum wire structures under high electric fields was recently reported by our group.<sup>12(b)</sup> Figure 8 shows the relative PL efficiency for the 1% Bu-PQ:PB PQ blend and the corresponding component polymers as a function of electric field. Both Bu-PQ and PB PQ show about 50% PL quenching at the electric field of  $1.5 \times 10^6$  V/cm which is the typical electric field of polymer LED operations (see Figure 6(b)). However, the 1% blend show only 30% quenching at the same field. This clearly reveals spatial confinement induced exciton stability in blends of Bu-PQ and PB PQ, indicating that exciton dissociation into free charge carriers is much more difficult in polymer blends. Thus, the probability for exciton to decay radiatively is increased and enhanced EL observed. Similar EFM-PL results were observed in the PTPQ:PB PQ system.

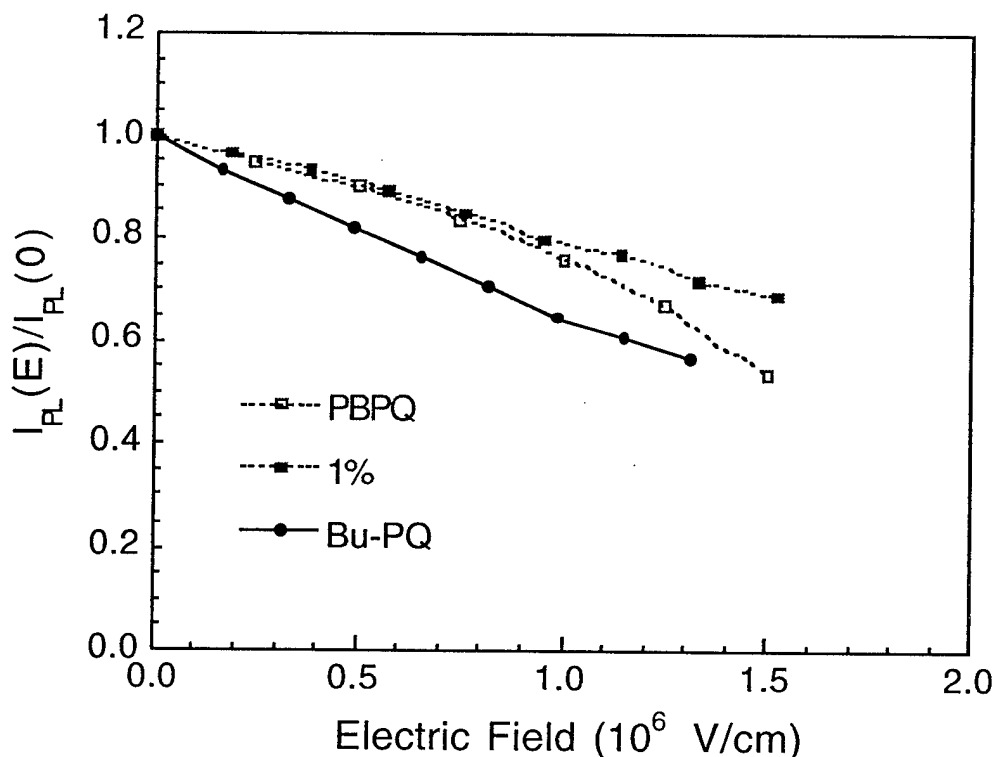


Figure 8. Electric field-induced PL quenching of Bu-PQ, PB PQ, and 1% blend.

## CONCLUSIONS

Electroluminescence of binary blends of conjugated polyquinolines was investigated by using four different model blend systems of PTPQ:PBPO, Bu-PQ:PBPO, Bu-PQ:Bu-PPQ, and Bu-PPQ:PPPQ. Four to thirty times enhancement of the EL of blends compared to the pure component polymers was observed. We have shown that spatial confinement of excitons in the dispersed component is critical to the observed enhancement of electroluminescence. Electric field-modulated photoluminescence spectroscopy confirmed that the observed EL enhancement originates from the spatial confinement of excitons which leads to improved electron-hole recombination efficiency and exciton stability. Thus, multicomponent polymer systems such as electroluminescent polymer blends are promising materials for developing efficient light-emitting diodes.

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