Chem. Mater. **1997,** *9,* 409−412

Finite Size Effects on Electroluminescence of Nanoscale Semiconducting Polymer Heterojunctions

Samson A. Jenekhe,* Xuejun Zhang, and
X. Linda Chen

Department of Chemical Engineering
University of Rochester
Rochester, New York 14627-0166

Vi-En Choong and Yongli Gao

Department of Physics and Astronomy
University of Rochester, Rochester, New York 14627

Bing R. Hsieh

Xerox Corporation, Webster, New York 14580

Received September 11, 1996
Revised Manuscript Received December 10, 1996

Many advances have been made in developing light emitting diodes (LEDs) of various colors from many π-conjugated polymers.[1−6] However, nearly all of the electroluminescent conjugated polymers investigated to date, such as poly(*p*-phenylenevinylene) (PPV), polythiophenes, poly(*p*-phenylenes), and their numerous derivatives, are *p-type (hole transport)* materials.[1,4−6] Dramatic improvements of polymer LED performance (lower turn-on voltage, higher efficiency, and higher luminance) and stability have been achieved by adding an *n-type (electron transport)* layer which typically consists of small molecules dispersed or covalently incorporated into nonconjugated polymers[1d,6] or a vapor deposited film. These improvements in bilayer or multilayer LEDs arise from the balanced injection and transport of both electrons and holes which are essential to the efficient production of singlet excitons. A few recent reports have also explored n-type conjugated polymers,[2,3] poly(diphenylquinoxaline) (PDPQ)[3] and poly(cyanoterephthalylidenes) (CN-PPVs),[2] as electron transport and emissive layers in bilayered electroluminescent devices. Electroluminescence emission from such n-type/p-type semiconducting polymer heterojunctions occurred from only the n-type layer,[2,3] and the lack of emission from *both layers* was attributed to the existence of a large barrier at the polymer/polymer interface or possible excitation energy transfer from the higher to the lower energy layer.[2]

We recently reported the observation of finite size effects on the photoconductivity of semiconducting polymer thin films.[7] It was shown that the quantum efficiency for charge photogeneration in a bilayer heterostructure containing a light absorbing semiconducting polymer thin film was increased by a factor of 3 when the film thickness of the conjugated polymer layer was reduced from 100 to 10 nm. Such a spatial confinement effect on photoconductivity originates from the small *exciton diffusion lengths* (∼5−20 nm) and the interfacial nature of the charge photogeneration process in the organic materials. Here, we report on several new n-type/p-type nanoscale semiconducting polymer heterojunctions and demonstrate novel finite size effects on electroluminescence and the electronic properties of the polymer/polymer heterojunction interfaces. The electroluminescence (EL) color from these polyquinoline/PPV heterojunctions was found to switch *reversibly* with the applied voltage; at low voltages, EL emission occurs from the n-type layer only whereas at higher voltages simultaneous EL emission from both layers is observed. Improved turn-on voltage, EL efficiency, and brightness were also observed in the heterojunction LEDs with bilayer emission compared to heterojunction devices with single-layer emission or to single-layer devices. The observed finite size effects on electroluminescence and interfacial charge transfer in the heterojunctions are accounted for in terms of the small and electric field-dependent *charge carrier ranges* in semiconducting polymers.

Several conjugated rigid-rod polyquinolines whose structures are shown in Figure 1 were used as the *n-type* (electron transport) layer. Their synthesis,[8] characterization,[8] and electrochemical,[9] optical[10] and nonlinear optical properties[11] have previously been reported. In particular, these and other conjugated polyquinolines were recently shown to exhibit excellent n-type (electron transport) properties.[9] The polyquinolines are also excellent high-temperature materials,[8] suggesting the possible improvement of stability and lifetime of LEDs if used as electron transport layers.[6]

The semiconducting polymer heterojunctions were prepared and investigated as sandwich structures between aluminum and indium−tin oxide (ITO) electrodes (Figure 1): Al/polyquinoline/PPV/ITO. The PPV thin films (25−130 nm) were deposited onto ITO-coated glass by spin coating of the sulfonium precursor[1a−d] in methanol solution followed by thermal conversion in vacuum (250 °C for 1.5 h). Thin films (30−100 nm) of the polyquinolines (PPQ, PPPQ, PBPQ, and PTPQ)[12] were

---

[1] (a) 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*, 539−541. (b) Brown, A. R.; Greenham, N. C.; Burroughes, J. H.; Bradley, D. D. C.; Friend, R. H.; Burn, P. L. ; Kraft, A.; Holmes, A. B. *Chem. Phys. Lett.* **1992**, *200*, 46−54. (c) Gusstafsson, G.; Cao, Y.; Treacy, G. M.; Klavetter, F.; Colaneri, N.; Heeger, A. J. *Nature* **1992**, *357*, 477−479. (d) Brown, A. R.; Bradley, D. D. C.; Burroughes, J. H.; Friend, R. H.; Greenham, N. C.; Burn, P. L. ; Kraft, A.; Holmes, A. B. *Appl. Phys. Lett.* **1992**, *61*, 2793−2795. (e) Grem, G.; Leditzky, G.; Ulrich, B.; Leising, G. *Adv. Mater.* **1992**, *4*, 36−37. (f) Ohmori, Y.; Uchida, M.; Muro, K.; Yoshino, K. *Jpn. J. Appl. Phys.* **1991**, *30*, L1938−L1940. (g) Bradley, D. D. C. *Synth. Met.* **1993**, *54*, 401−415.

[2] Greenham, N. C.; Moratti, S. C.; Bradley, D. D. C.; Friend, R. H.; Holmes, A. B. *Nature* **1993**, *365*, 628−630.

[3] Yamamoto, T.; Inoue, T.; Kanbara, T. *Jpn. J. Appl. Phys.* **1994**, *33*, L250−L253.

[4] Colvin, V. L.; Schlamp, M. C.; Alivisatos, A. P. *Nature* **1994**, *370*, 354−357.

[5] Berggren, M.; Inganäs, O.; Gustafsson, G.; Rasmusson, J.; Andersson, M. R.; Hjertberg, T.; Wennerström, O. *Nature* **1994**, *372*, 444−446.

[6] Strukelj, M.; Papadimitrakopoulos, F.; Miller, T. M.; Rothberg, L. J. *Science* **1995**, *267*, 1969−1972.

[7] Zhang, X.; Jenekhe, S. A.; Perlstein, J. *Chem. Mater.* **1996**, *8*, 1571−1574.

[8] (a) Agrawal, A. K.; Jenekhe, S. A. *Macromolecules* **1991**, *24*, 6806−6808. (b) Agrawal, A. K.; Jenekhe, S. A. *Macromolecules* **1993**, *26*, 895−905. (c) Agrawal, A. K.; Jenekhe, S. A. *Chem. Mater.* **1993**, *5*, 633−640.

[9] Agrawal, A. K.; Jenekhe, S. A. *Chem. Mater.* **1996**, *8*, 579−589.

[10] Agrawal, A. K.; Jenekhe, S. A. *Chem. Mater.* **1992**, *4*, 95−104.

[11] (a) Agrawal, A. K.; Jenekhe, S. A.; Vanherzeele, H.; Meth, J. S. *J. Phys. Chem.* **1992**, *96*, 2837−2843. (b) Agrawal, A. K.; Jenekhe, S. A.; Vanherzeele, H.; Meth, J. S. *Chem. Mater.* **1991**, *3*, 765−768.

[12] The full names of the polyquinolines of Figure 1 are poly[2,6-(4-phenylquinoline)] (PPQ); poly[2,2′-(*p*-phenyl)-6,6′-bis(4-phenylquinoline)] (PPPQ); poly[2, 2′-(*p*,*p*′-biphenyl)-6,6′-bis(4-phenylquinoline)] (PBPQ); poly[2,2′-(2,5-thiopheneyl)-6,6′-bis(4-phenylquinoline)] (PTPQ).

S0897-4756(96)00474-7 CCC: $14.00

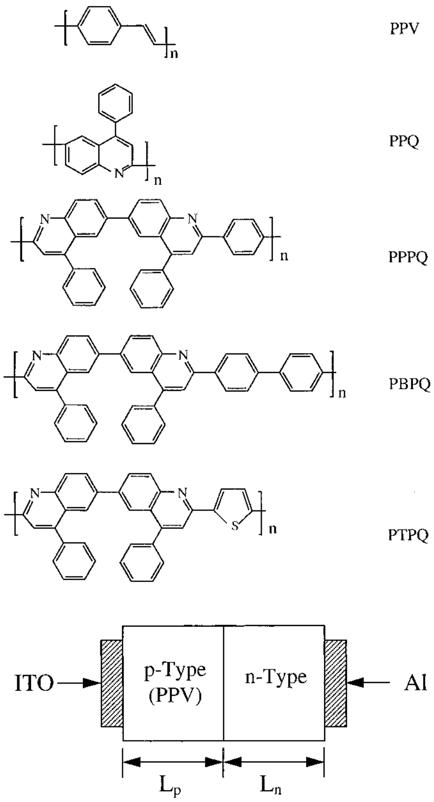

Figure 1. Electroluminescent p-type/n-type semiconducting polymer heterojunction device and chemical structures of emissive p-type and n-type π-conjugated polymers.

spin coated from their formic acid solutions onto the PPV layer and dried at 80 °C in vacuum overnight. Because PPV does not dissolve or swell in formic acid, heterojunctions with relatively sharp polymer/polymer interfaces were obtained. 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. These film thicknesses of bilayers relative to single layers of the component polymers further confirmed that the polymer/polymer interfaces were relatively sharp. Additional reasons for achieving such sharp interfaces include: the relatively short solution contact time (<30 s) and high solvent evaporation rate during spin coating, and the rodlike nature of the polyquinolines which preclude ready diffusion into the underlying PPV film. Finally, 100−130 nm aluminum electrodes were vacuum (10^{-5} Torr) evaporated onto the resulting polymer bilayers. Electroluminescence spectra were obtained by using a calibrated Photo Research Model PR-60 photocolorimeter. The brightness of LEDs was measured by using a silicon avalanche photodiode. The quantum efficiencies of the diodes were estimated by using procedures similar to that previously reported.[13] All the fabrication and measurements were done under ambient laboratory conditions. The photoluminescence (PL) spectra of the single layers and bilayers whose electroluminescence is reported here were also investigated. The PL spectra of polyquinolines/PPV bilayers were found to be mere superpositions of those of the components, implying absence of excitation energy transfer or exciplex formation.

The electroluminescence from a PPQ(67 nm)/PPV(25 nm) heterojunction was orange/red (Figure 2a) at all forward bias voltages in the range of 10−30 V; the turn-on voltage of the diode was 10 V. This EL spectrum was identical with that of the single-layer device (ITO/PPQ/Al). This means that the emission zone of this bilayer LED is located in the n-type layer and that charge transfer across the PPQ/PPV interface is *unipolar* at all bias voltages. However, the characteristics of a similar PPQ(40 nm)/PPV(25 nm) heterojunction device were dramatically different when the PPQ layer thickness was reduced from 67 to 40 nm. At forward bias voltages of 8−10 V an orange emission characteristic of PPQ electroluminescence is observed (Figure 2b). At higher voltages (13−20 V), a relatively broadband emission from both layers is observed and because the PPV emission ($\lambda_{max} = 504$, 544 nm) is dominant the color perceived was green. These EL observations on the PPQ(40 nm)/PPV(25 nm) heterojunction imply that at low bias voltages the emission zone is confined to the n-type layer and hence that charge transfer across the PPQ/PPV interface is *unipolar* (hole transfer) at low voltages. However, at higher voltages charge transfer at the PPQ/PPV interface becomes *bipolar* (both holes and electrons cross the interface), facilitating bilayer EL emission.

A PPQ(33 nm)/PPV(62 nm) heterojunction device with a thicker p-type layer exhibited characteristics that were different from the two previous PPQ/PPV bilayers. At low bias voltages, an orange EL characteristic of PPQ layer is observed (Figure 2c). However, a shoulder at ~506 nm due to emission from the PPV layer is already evident in the EL spectra at low voltages (10−15 V). At higher voltages (>16 V), emission from the PPV layer increases and eventually becomes dominant, giving rise to green color electroluminescence. A further increase of the PPV layer thickness while keeping the PPQ layer at 33 nm gave the EL spectra shown in Figure 2d for the PPQ(33 nm)/PPV(117 nm) heterojunction device. In this case, simultaneous emission from both layers is observed at all forward bias voltages. A relatively broad emission band (yellowish green EL color) with about equal emission intensities from PPQ and PPV layers is observed at 20 V. Green electroluminescence is seen at higher voltages as the contribution of the PPV layer to the EL intensity becomes dominant. Only green electroluminescence characteristic of the PPV EL spectrum was observed from a PPQ(30 nm)/PPV(130 nm) heterojunction at all forward bias voltages (20−27 V), suggesting that the limiting case of *unipolar electron transfer* at the PPQ/PPV interface and hence of a *single-layer emission* from a bilayer device has been reached with the relatively thick PPV layer. The EL color switching of the heterojunction LEDs with applied voltage was reversible as confirmed by identical EL spectra and intensity obtained with *increasing* or *decreasing* forward bias voltages (Figures 2b−d). Similar results of voltage tunability of electroluminescence color were obtained with PPPQ/PPV and PBPQ/PPV heterojunctions in which reversible orange to green switching was observed at ~15−17 V when the n-type layer thickness was in the range of 30−40 nm. With thicker films (75−85 nm) of PPPQ and PBPQ the heterojunctions showed only orange color EL which is characteristic of the n-type layer in these devices.

---

[13] Greenham, N. C.; Friend, R. H.; Bradley, D. D. C. *Adv. Mater.* **1994**, *6*, 491−494.

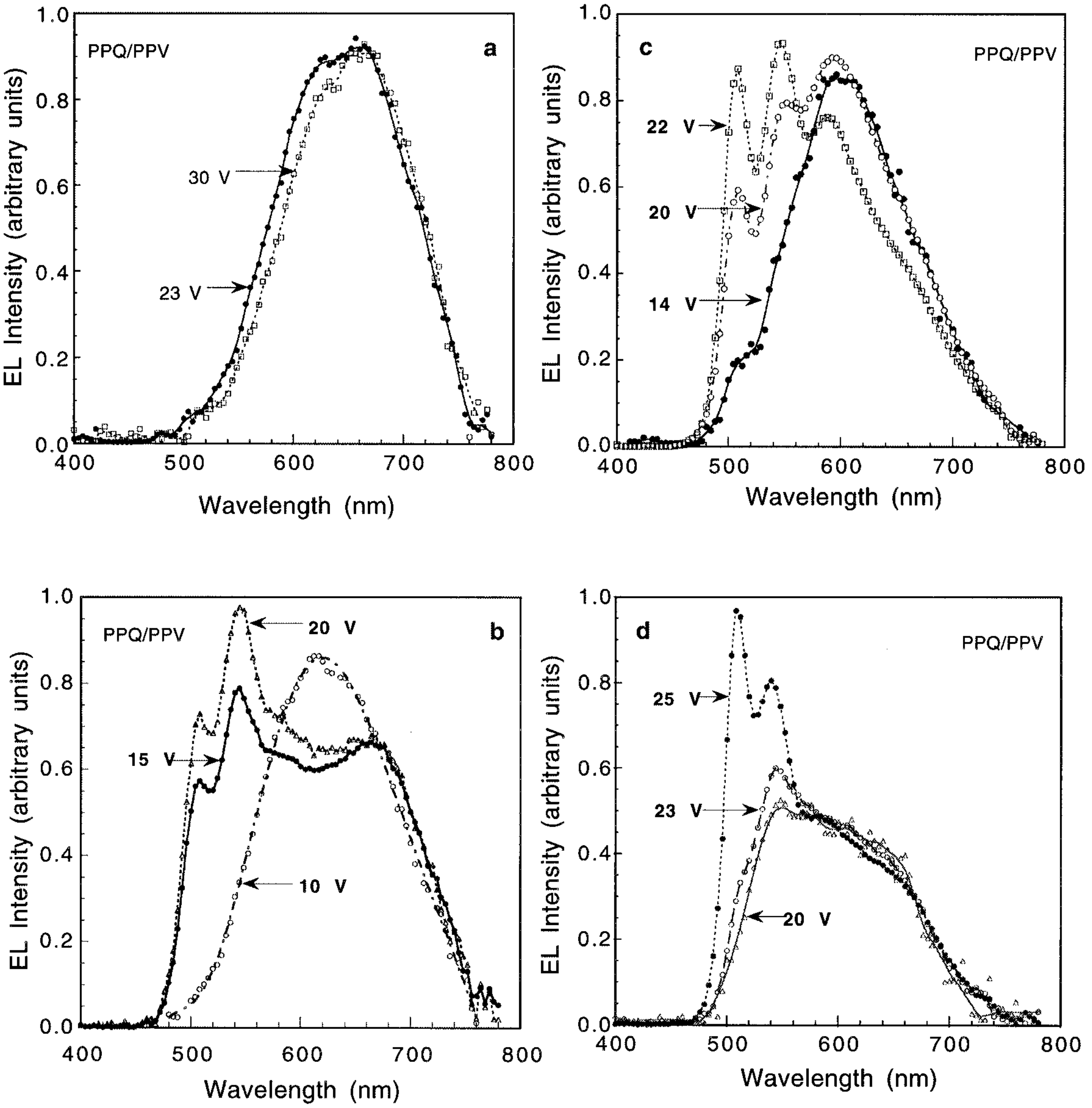

Figure 2. Electroluminescence spectra of PPQ/PPV heterojunction devices as a function of layer thicknesses and forward bias voltages: (a) EL spectra from a PPQ(67 nm)/PPV(25 nm) diode; (b) EL spectra from a PPQ(40 nm)/PPV(25 nm) diode; (c) EL spectra from a PPQ(33 nm)/PPV(62 nm) diode; (d) EL spectra from a PPQ(33 nm)/PPV(117 nm) diode.

These heterojunction EL spectra, which can be deconvoluted into the EL spectra of the constituent layers, demonstrate that the recombination and emission zones within the polymer heterojunctions, and hence the colors from the LEDs, can be regulated by the relative layer thicknesses (L_p, L_n) of the n-type/p-type bilayers (Figure 1). In this way heterojunction LEDs can be designed to exhibit one-color electroluminescence from either the p-type or the n-type layer or bilayer EL emission or both. These remarkable finite size effects in the nanoscale region (25−130 nm) are related to the intrinsic charge transport properties of the semiconducting polymers as well as the behavior of the n-type/p-type polymer/polymer heterojunction interface. The fact that charge transfer at the heterojunction interface of the same pair of semiconducting polymers can vary from *unipolar hole transfer* at all fields to *unipolar hole transfer/bipolar (electron and hole) transfer* depending on the applied field to *unipolar electron transfer* at all fields by variation in layer thicknesses suggests that energy band edge offset due to differences in electron affinity (EA) and ionization potential (IP) of PPV and the n-type polyquinolines cannot account for the spatial confinement effects. EA values of the series of polymers based on estimates from cyclic voltammetry were in the range 2.42−2.62 eV[9] which are smaller than the 2.7 eV reported for PPV.[14] Similarly, estimated IP values of the polymers were in the range 5.05−5.28 eV[9] compared to 5.1 eV for PPV.[14] Based on these zero-field band edge offsets there are no barriers to electron transfer at the polyquinoline/PPV heterojunction interfaces whereas barriers to hole transfer are small (ΔIP ~ 0.13−0.18 eV).

We propose that the observed finite size effects on the electroluminescence of these nanoscale polyquinoline/PPV heterojunctions arise from limitations imposed on charge transport by the *charge carrier ranges* in the semiconducting polymers. The *range* of a charge carrier injected into a material is the mean distance traveled before trapping or recombination. Although the ranges of electrons (x_e) and holes (x_h) in semiconducting polymers are rarely known, just as the related mobilities of

---

(14) Eckhardt, H.; Shacklette, L. W.; Jen, K. Y.; Elsenbaumer, R. L. *J. Chem. Phys.* **1989**, *91*, 1301−1315.

electrons (μ_e) and holes (μ_h), they can be expected to be in the nanoscale-size region and also field-dependent since the range is approximately the product of mobility, carrier lifetime, and electric field ($x_e = \mu_e\tau_e E$, $x_h = \mu_h\tau_h E$).[15,16] By comparing the ranges of the majority carriers in the polyquinolines (electrons) and PPV (holes) to the layer thicknesses (L_n, L_p) of the heterojunctions, the finite size effects can be clearly understood. The observed unipolar hole transfer and associated emission from the n-type layer at all fields (e.g. Figure 2a) arise from the combination of an n-layer thickness that is greater than the electron range and a p-layer thickness that is less than the hole range ($L_n > x_e$, $L_p < x_h$). Similarly, the observed unipolar electron transfer and associated EL emission from the p-layer at all fields in PPQ(30 nm)/PPV(130 nm) heterojunction are consequences of the combination of an n-layer that is thinner than the electron range and a p-layer that is thicker than the hole range ($L_n < x_e$, $L_p > x_h$). It is when the n-layer and p-layer thicknesses are comparable or less than the electron and hole ranges, respectively ($L_n \leq x_e$, $L_p \leq x_h$), that the novel feature of combined unipolar and bipolar charge transfer and associated voltage tunable electroluminescence colors are obtained. From these considerations and our results we estimate the range of holes in PPV to be ~120 nm and the range of electrons in the polyquinolines investigated here to be between 40 and 70 nm. These values of carrier ranges in semiconducting polymers are orders of magnitude smaller than carrier ranges in typical inorganic semiconductors.[16,17] The qualitative features of these p−n semiconducting polymer heterojunctions are also dramatically different from inorganic semiconductor p−n heterojunctions.[17]

Because our initial focus on these semiconducting polymer heterojunction LEDs has been on exploring their unusual emission characteristics and the underlying finite size effects, the quantitative performance of the devices such as quantum efficiency, brightness, and current density has not been optimized. Nevertheless, all the heterojunction LEDs with voltage tunable colors had significantly better performance than the single-layer devices or even bilayer LEDs with only a *single-layer emission*. For example, the single-layer devices Al/PPQ(40 nm)/ITO and Al/PPV(62 nm)/ITO had EL efficiency and luminance of 0.007 and 0.006% and 0.32 and 7 cd/m^2, respectively. The EL efficiency and luminance of various PPQ/PPV heterojunction LEDs were respectively 0.13% and 40−100 cd/m^2. In general, we found that the EL efficiency and luminance of the heterojunction devices were about factors of 10−40 enhanced compared to the single-layer devices. Also, the heterojunction LED performance for a given pair of emissive semiconducting polymers, e.g., PPQ/PPV, were found to vary by factors of up to 10−15 as the layer thicknesses were varied. The turn-on voltages and the corresponding electric fields of the polyquinoline/PPV heterojunctions were up to a factor of 2 smaller than the single-layer polyquinoline diodes (Figure 3). These results suggest that finite size effects also strongly influence the performance of the heterojunction devices.

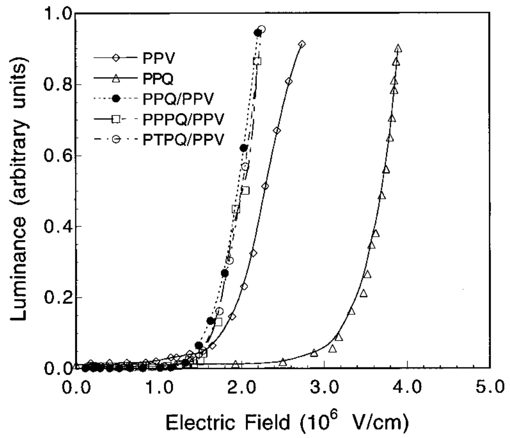

Figure 3. Luminance versus electric field for some n-type/p-type semiconducting polymer heterojunction LEDs with voltage tunable colors along with some single-layer devices.

In summary, we have prepared several new nanoscale (25−130 nm) n-type/p-type heterojunctions of semiconducting polymers and observed finite size effects on their electroluminescence. Our results demonstrate that π-conjugated polyquinolines can be used as both emissive and electron transport layers in light-emitting devices. The polyquinolines/PPV heterojunction light-emitting diodes with appropriate nanoscale layer thicknesses were found to switch colors (orange/red ↔ green) reversibly with applied forward bias voltage and to exhibit enhanced performance compared to the single-layer devices or bilayer devices with only single-layer emission. The finite size effects on these heterojunctions were explained in terms of charge carrier range-imposed confinement of charge carriers in the semiconducting polymers. These results suggest that p−n heterojunctions of semiconducting polymers are qualitatively different from those of inorganic semiconductors. Finite size effects in semiconducting polymer heterojunctions also have implications for other electronic and optoelectronic applications such as photovoltaic cells, field-effect transistors, and photodetectors.

Acknowledgment. This research was supported by the Office of Naval Research and the National Science Foundation (CTS-9311741, CHE-9120001).

CM960474Q

---

(15) Antoniadis, H.; Abkowitz, M. A.; Hsieh, B. R. *Appl. Phys. Lett.* **1994**, *65*, 2030−2032.

(16) Allen, J. W. *J. Lumin.* **1994**, *60−61*, 912−915.

(17) Kittel, C. *Introduction to Solid State Physics*, 6th ed.; John Wiley: New York, 1986; Chapter 19.