Research Paper

Volume : 4 | Issue : 12 | December 2015 • ISSN No 2277 - 8179

Electroluminescence from Blends of PQ

Engineering

KEYWORDS :

Miss. Pratima V. Damre Government College of Engineering and Research Awsari(khurd) Taluka-Ambegao, Dist-Pune.

Dr.V. M. Raut Government Vidarbh Institute of Science and Humanities,Amravati

ABSTRACT

Electroluminescence efficiency and brightness of light-emitting diodes fabricated from binary blends of conjugated polyquinolines was observed compared to devices made from the homopolymers. Blends of poly (2,2'- (2,5-thienylene) - 6,6'-bis(4-phenylquinoline)) (PTPQ) and poly (2,2 '(biphenylene) -6,6'-bis (4-phenylquinoline)) (PBPQ), for example, had EL efficiency and luminance of up to a factor of 30 enhancement. Energy transfer was negligible in all four binary blend systems investigated. The electrical properties of the diodes and electric-field-modulated photoluminescence spectroscopy results confirmed that the enhancement of electroluminescence in the blends originated from spatial confinement of excitons which leads to increased exciton stability and electron-hole recombination efficiency. Voltagetunable and composition-tunable multicolor electroluminescence was observed in the polymer blend devices. The observed composition-dependent new emission bands and enhanced fluorescence lifetimes in the blends were suggested to originate from exciplex formation and molecular miscibility between the blend components. These results demonstrate new phenomena in the electroluminescence and photophysics of multicomponent conjugated polymers.

Introduction –

Conjugated polymers are molecular semiconductors with important electronic, optoelectronic, and photonic properties which are currently being exploited in various device applications. As such, blends of conjugated polymers are expected to be supramolecular materials or alloys in which novel properties and phenomena not found in the homopolymers can emerge as a result of synergistic intermolecular interactions between components of the mixture, spatial confinement effects, and self-organization. In principle, blends of conjugated polymers are thus very promising for the development of optimal materials for electronic, optoelectronic, and photonic applications. Recent studies of blends of conjugated polymers have indeed shown them to exhibit novel supramolecular electronic, optoelectronic, and photonic properties such as optical absorption modulation,[2] photoinduced charge transfer,[2,3] bipolar conductivity,[4] enhanced photoconductivity,[3,5] efficient energy transfer,6 enhanced electroluminescence,[7] and enhanced nonlinear optical properties.[8] Construction of organic quantum-well nanostructures, such as quantum wires and quantum boxes, by self-organization of blends of a block conjugated copolymer with a parent conjugated homopolymer9 and facilitation of stimulated emission[10] and low-threshold amplified spontaneous emission[11] in blends of conjugated polymers have also been demonstrated. Electroluminescence (EL) from blends of conjugated polymers has been described in several recent reports.[7,12] Voltage-tunable electroluminescence color was observed in phase-separated blends of several polythiophene derivatives having different emission colors.[12] Phase separation of the blends on the 50-200 nm scale, which is comparable to or larger than the emitter thickness in the devices, was essential to the multicolor LED emission.[12] 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-cyclohexylthiophene),[13] from binary blends of poly(2-methoxy-5-(2′-ethylhexoxy)-1,4-phenylenevinylene)) (MEH-PPV) with an alkoxy(trifluoromethyl)stilbene-substituted poly(methyl acrylate) derivative (CF3-PMA),[12] from blends of a ladder-type poly(pphenylene) (m-LPPP) with poly(perylene-co-diethylbenzene) (PPDB),[13] and from ternary blends of polyquinolines. Enhancement in EL quantum efficiency and luminance of LEDs made from blends, compared to the component polymers, has been reported. Blends of poly(3-hexylthiophene) (P3HT) and MEH-PPV,[7] blends of MEH-PPV, and a conjugated-nonconjugated multiblock copolymer (CNMBC), poly(1,3-propanedioxy-1,4-phenylene-1,2-ethylene(2,5-bis(trimethylsilyl)-1,4-phenylene)1,2-ethenylene-1,4-phenylene),[7] were reported to have enhanced EL efficiency. The mechanism of the observed EL enhancement was attributed to Forster-type energy transfer from MEH-PPV to P3HT or from CNMBC to MEH-PPV. In addition to excitation energy transfer, several other processes or mechanisms are possible in the photophysics and EL of polymer blends depending on the electronic structures of the component conjugated polymers. Ground-state charge transfer or complex formation,4 excited-state complex (exciplex) formation,[14] photoinduced electron transfer,[2,3] and exciton confinement9b are possible. However, depending on the relative lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) levels of polymers A and D (here we assume that the HOMO-LUMO gaps are such that EgD > EgA) in a blend (denoted A:D), the dominant process may be different in the three cases of HOMO/LUMO level pairs illustrated in Figure 1. These diverse photophysical and charge-transfer processes are yet to be fully delineated and understood in blends of electroluminescent conjugated polymers. In a previous paper, we investigated the roles of polymer/polymer interfaces in the electroluminescence of multicomponent conjugated polymer systems by using bilayer thin films.

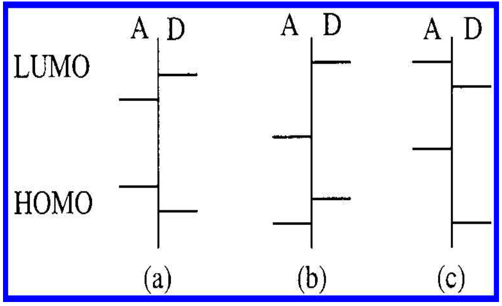
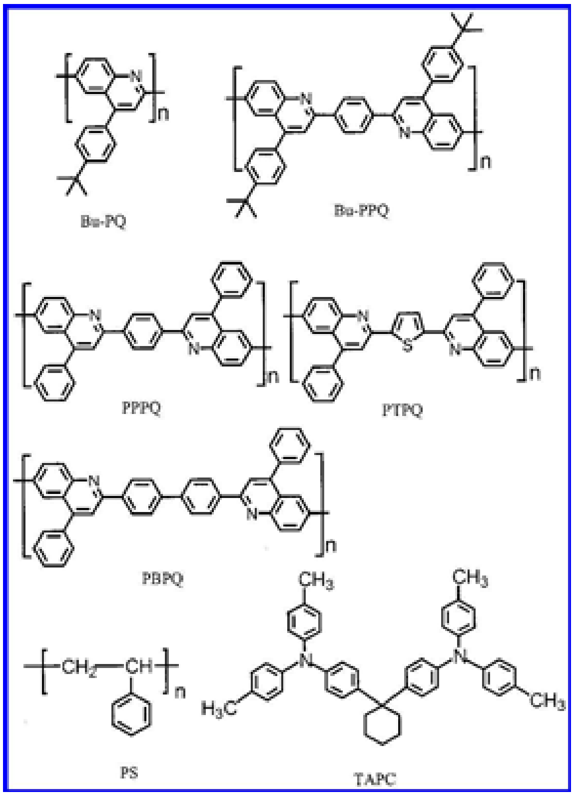


Figure 1-Schematic illustration of some possible relative energy levels of polymers Aand D in a binary polymer blend A:D $E_g^D > E_g^A$

Experimental section

Materials. All the polyquinolines used in this study were previously synthesized in our laboratory. The synthesis, characterization, thin film processing, optical and nonlinear optical properties, electrochemistry, photoconductivity, and electro- luminescence of these and many other polyquinolines were previously reported by our group. The polyquinolines used in this study had intrinsic viscosities of 3—12 dL/g, which were measured in 0.1 mol % di-m-cresyl-phosphate / m-cresol at 25 °C or in methanesulfonic acid at 30 °C, indicating that they are high molecular weight polymeric materials. Since all the polyquinolines are good electron transport (n-type) and emissive materials, [2-3]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 (PS).[17a] TAPC was provided by Eastman Kodak Co. (Rochester, NY). PS with a molecular weight (M_n) of ~200 000 was obtained from Polysciences. The molecular structures of the materials used in this study are shown in Chart 1.

Chart 1.



Preparation of Blends and Thin Films. Binary blends of polyquinolines were prepared by dissolving the binary mixtures in formic acid in which both polymers are very soluble. The resulting solutions (0.3—0.4 wt % total polymers) were homogeneous. Compositions of blends (A:D) in this paper refer to weight percentage of polymer A. Four series of blend compositions were prepared in this study. For example, 0.1,1, 5, 10, 20, 30, and 50 wt % PTPQ:PBPQ blends were prepared. Since PTPQ and PBPQ have close repeat unit molecular weights (488.6 for PTPQ and 558.7 for PBPQ), the concentrations of PTPQ in wt % and in mol % are close.

Although prior studies of blends of various conjugated polymers in[2,4,6] our group have used complexation mediated processing, [12]all thin films of the homopolymers or blends reported here 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 a vacuum to remove any residual solvent. Blend films (25—35 nm thick) were homogeneous and showed excellent optical transparency. No visible phase separation was observed. The good miscibility between polyquinolines is due to their structural similarities. Because of a lack of contrast, attempts to use transmission electron microscopy (TEM) to probe the morphology of these polyquinoline blends were not successful. Since PBPQ and PTPQ emit orange and red color, respectively, we also applied an Olympus BX60 fluorescence microscope (Olympus America, Melville, NY) to investigate the morphology of blends. No features were resolved, indicating homogeneity and good miscibility in blends or that the phase separation domains, if any, are less than the resolution of the fluorescence microscope (~500 nm). Miscibility on a much smaller scale was subsequently indicated from photoluminescence and electroluminescence studies of the blends.

Result and Discussion-

Electroluminescence. The EL spectra of polyquinolines and their blends at low bias voltages were found to be similar to the corresponding PL spectra. At higher forward bias voltages, EL spectra of blends were significantly blue-shifted from the corresponding PL spectra. Representative EL spectra of PTPQ, PBPQ, and some of their blends are shown in Figure 2. The EL spectrum of PTPQ in Figure 2b is identical to the PL spectrum in Figure 5a, showing an emission peak at 622 nm. This suggests that the EL and PL emissions of this polymer originate from the same excited state. PBPQ showed an EL emission peak at 557 nm at a bias voltage of 8 V. The EL spectra of PTPQ:PBPQ blends (0.1, 5,10, and 30%) are also shown in Figure 2. It was found that the EL spectra of both PBPQ and the 0.1% blend varied with the bias voltage. In the case of PBPQ (Figure 2a), the EL emission peak shifted from 557 nm (yellow) at 8 V to 520 nm (green) at 13 V, and the EL intensity from the 450 nm blue band increased with increasing bias voltage.The most striking EL blue shift with bias voltage was observed in the 0.1% blend (Figure 2c). The EL emission peak of the 0.1% blend was found to go from 547 nm (yellow) to 500 nm (blue-green) when the applied bias voltage was changed from 8 to 15 V. The 0.1% blend showed a much more dramatic increase in the EL intensity from the blue band with increasing voltage than PBPQ. For example, at 15 V, the EL intensity of the blue band (445 nm) is almost the same as that of the 500 nm band. The blue shift of the EL spectrum with increasing bias voltage was also observed in the 1-5% blends. Voltage tunability of the EL emission was negligible in the 10-50% blends. The enhanced EL emission in the blue band is due to the enhanced emission from higher energy states, such as the PTPQ single chains in which excitons are spatially confined. These blend EL spectra results are to be contrasted with those observed in binary blend systems exhibiting energy transfer where enhanced emission from the dispersed, minority, and lower-energy component is usually observed at the expense of the higher-energy matrix.

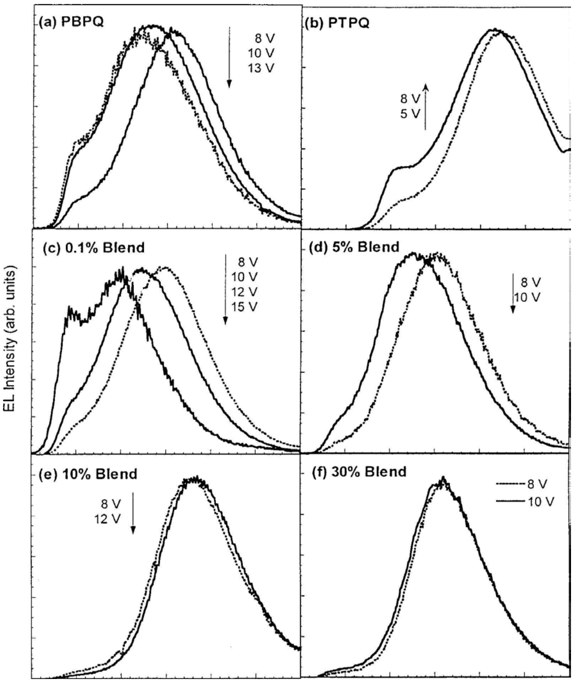


Figure 2. EL spectra of a] PBPQ, b] PTPQ, c] 0.1% blend, d] 5% blend, e] 10% blend and f] 30%PTPQ:PBPQ blend system

Conclusions

Electroluminescence of binary blends of conjugated polyquinolines was investigated using four different model blend systems of PTPQ:PBPQ, Bu-PQ:PBPQ, Bu-PQ:Bu-PPQ, and PPPQ:Bu-PPQ. A 3-30 times enhancement of EL efficiency and LED brightness of the blends compared to those of the homo- polymers was observed.

Acknowledgement

This research was supported by the Department of Chemistry, Government Vidarbh Institute of Science and Humanities, Amravati.

REFERENCE

[1] [a] P.D. Sybert, W.H. Beever, J.K. Stille, Macromolecules 1981, | 14, 493. [b] E.K. Zimmerman, J.K. Stille, Macromolecules 1985, | 18, 321. [c] M.W. Pelter, J.K. Stille, Macromolecules 1990, 23, | 2418. | [2] [a] A.K. Agrawal, S.A. Jenekhe, Chem. Mater. 1992, 4, 95. [b] | A.K. Agrawal, S.A. Jenekhe, Macromolecules 1993, 26, 895. | [3] A.K. Agrawal, S.A. Jenekhe, Chem. Mater. 1996, 8, 579. | [4] M.A. Abkowitz, M. Stolka, H. Antoniadis, A.K. Agrawal, S.A. | Jenekhe, Solid State Commun. 1992, 83, 937. | [5] A.K. Agrawal, S.A. Jenekhe, H. Vanherzeele, J.S. Meth, J. Phys. | Chem. 1992, 96, 2837. | [6] S.A. Jenekhe, X. Zhang, X.L. Chen, V.-E. Choong, Y. Gao, B.R. | Hsieh, Chem. Mater. 1997, 9, 409. | [7] D.M. Sutherlin, J.K. Stille, Macromolecules 1985, 18, 2669. | [8] G.S. Skinner, J.A. Gladner, R.F. Heitmiller, J. Am. Chem. Soc. | 1951, 73, 2230. | [9] R.B. Davis, L.C. Pizzini, J. Org. Chem. 1960, 25, 1884. | [10] S.A. Jenekhe, J.A. Osaheni, Science 1994, 265, 765. | [11] J.A. Osaheni, S.A. Jenekhe, J. Am. Chem. Soc. 1995, 117, 7389. | [12] J.H. Burroughes, D.D.C. Bradley, A.R. Brown, R.N. Marks, K. | MacKay, R.H. Friend, P.L. Burn, A.B. Holmes, Nature 1990, | 347, 539. | [13] N.C. Greenham, R.H. Friend, D.C.C. Bradley, Adv. Mater. 1994, | 6, 491. |