

**FINAL TECHNICAL REPORT**

**AASERT 92 - SYNTHESIS AND PROPERTIES OF COMPLEX  
POLYARYLENE VINYLENES**

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**FRANK E. KARASZ**

**DEPARTMENT OF POLYMER SCIENCE & ENGINEERING**

**UNIVERSITY OF MASSACHUSETTS**

**AMHERST, MA 01003**

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13. ABSTRACT (Maximum 200 words) A series of polymeric chromophores has been synthesized for use in polymeric light emitting diodes. These materials are based on the concept of alternating block copolymers containing a "soft" oligomethylene sequence and a "hard" chromophoric block based on an oligo arylene vinylene structure. Furthermore these materials can be blended to improve exciton confinement and enhance electroluminescence. For example, in a 1:1 weight ratio blend of a fully conjugated poly(2,5-diheptoxy-p-phenylene vinylene-alt-2,5-dimethoxy-p-phenylene) (DHDMPV) with a conjugated-nonconjugated multiblock copolymer (CNMBC) poly(1,8-octanedioxy-2,6-dimethoxy-1,4-phenylene-1,2-ethenylene-1,4-phenylene-1,2-ethenylene-1,4-phenylene-1,2-ethenylene-3,5-dimethoxy-1,4-phenylene), efficient energy transfer both in photoluminescence (PL) and electroluminescence (EL) from CNMBC to DHDMPV was observed by measuring the absorption, PL, and EL spectra of DHDMPV, CNMBC, and of their blend at room temperature (RT) and at 77K. The external EL quantum efficiency (0.03% photon/electron) and the brightness (400 cd/m <sup>2</sup> ) of the DHDMPV EL device was increased, respectively, to 0.12% photon/electron and 800 cd/m <sup>2</sup> , by blending. The measurements show this is achieved by confinement of injected holes and electrons in the blend resulting in enhanced probability of exciton formation. This confinement of injected charge carriers by blending is consistent with a large body of experimental results obtained here.				
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## ABSTRACT

A series of polymeric chromophores has been synthesized for use in polymeric light emitting diodes. These materials are based on the concept of alternating block copolymers containing a "soft" oligomethylene sequence and a "hard" chromophoric block based on an oligo arylene vinylene structure. Furthermore these materials can be blended to improve exciton confinement and enhance electroluminescence. For example, in a 1:1 weight ratio blend of a fully conjugated poly(2,5-diheptoxy-*p*-phenylene vinylene-alt-2,5-dimethoxy-*p*-phenylene) (DHDMPV) with a conjugated-nonconjugated multiblock copolymer (CNMBC) poly(1,8-octanedioxy-2,6-dimethoxy-1,4-phenylene-1,2-ethenylene-1,4-phenylene-1,2-ethenylene-1,4-phenylene-1,2-ethenylene-3,5-dimethoxy-1,4-phenylene), efficient energy transfer both in photoluminescence (PL) and electroluminescence (EL) from CNMBC to DHDMPV was observed by measuring the absorption, PL, and EL spectra of DHDMPV, CNMBC, and of their blend at room temperature (RT) and at 77K. The external EL quantum efficiency (0.03% photon/electron) and the brightness (400 cd/m<sup>2</sup>) of the DHDMPV EL device was increased, respectively, to 0.12% photon/electron and 800 cd/m<sup>2</sup>, by blending. The measurements show this is achieved by confinement of injected holes and electrons in the blend resulting in enhanced probability of exciton formation. This confinement of injected charge carriers by blending is consistent with a large body of experimental results obtained here.

Polymer based light emitting diodes (PLEDs) are typically a sandwich structure in which the conjugated polymer light-emitting layer is between an anode, such as indium tin oxide (ITO), and a cathode, such as calcium. Positive charge carriers (holes) and negative charge carriers (electrons) are injected from the respective electrodes. The injected holes in the valence band and electrons in the conduction band move through the conjugated polymer layer under the influence of the applied electrical field and either annihilate to form singlet or triplet excitons in the polymer layer resulting in electroluminescence, or pass through the polymer layer to the opposite electrode and are dissipated in a non-radiative process. To improve efficiency and brightness conjugated polymers with a high intrinsic quantum efficiency of photoluminescence should be used. The PL quantum efficiency of these macromolecules is limited by structure defects, impurities, and the dimension and scope of exciton migration. PPV and some PPV derivatives exhibit a good PL quantum efficiency, but there is as yet no satisfactory explanation for the relation between quantum efficiency of PL and molecular structures of conjugated polymers.

A second method for improving efficiency is to use appropriate high work function materials as the anode and low work function materials as the cathode to improve carrier injection flux, while a third method is to more efficiently confine injected holes and electrons in the conjugated polymer layer to increase the recombination probability, thereby changing the ratio between radiative and non-radiative processes. To confine injected holes and electrons in the polymer layer additional materials with appropriate conduction and valence band offsets at the

semiconductor heterojunction interfaces may be used. Typically therefore a hole transport layer (HTL) between the anode and the light-emitting layer to block the movement of electrons to the anode and an electron transport layer (ETL) between the cathode and light-emitting layer to block the movement of injected holes to the cathode are used.

We have developed a methodology for confining injected charge carriers by blending electroactive polymers in which external EL quantum efficiency and brightness have been typically improved by an order of magnitude.

The blend of the conjugated-nonconjugated multiblock copolymer (CNMBC) poly(1,8-octanedioxy-2,6-dimethoxy-1,4-phenylene-1,2-ethenylene-1,4-phenylene-1,2-ethenylene-1,4-phenylene-1,2-ethenylene-3,5-dimethoxy-1,4-phenylene) and the fully conjugated polymer poly(2,5-diheptoxy-*p*-phenylenevinylene-2,5-dimethoxy-*p*-phenylenevinylene) (DHDMPV) provide an example. These polymers have good solubility in most solvents and excellent film formation. The EL devices were fabricated using the conventional sandwich structure. Indium tin oxide (ITO) and Al were used as the anode and the cathode, respectively. DHDMPV and a blend of 1:1 weight ratio of CNMBC with DHDMPV were used as the light-emitting layers, and were spin-coated onto ITO glass from chloroform solutions in a nitrogen gas-filled glovebox. The thickness of the spin-coated films of DHDMPV and the blend was 1100 Å measured with both a Dektak surface profiler and ellipsometry. The Al cathode was vacuum-deposited at  $2 \times 10^{-6}$  Torr. The pixel area is 6 mm<sup>2</sup>. The voltage applied to the EL devices and the current through the EL devices were monitored

with FLUKE 8020B and DMM-200 JDR instrument multimeters. The EL was observed through the ITO glass substrate. EL brightness was measured with a commercial radiometer/photometer model IL 1400A( International Light Inc.).

To explore the EL improvement in DHDMPV devices by blending with CNMBC we compared the i-V data for the blend EL device with that of the single component DHDMPV EL device. This comparison showed that the onset voltage of the DHDMPV device has been decreased by a factor of five by CNMBC blending. The EL intensity of the DHDMPV and of the blend EL device as a function of current shows that for the same EL intensity the current density in the blend EL device is five times lower than that of the DHDMPV EL device.

The lower current at equal intensities of the blend compared to the DHDMPV EL device implies that there is a confinement of injected charge carriers and an increase in the recombination probability of injected holes from the anode and electrons from the cathode in DHDMPV by blending. The blend EL device has a similar EL behavior, in terms of color output and reverse bias operation as does the DHDMPV EL device. It was found that the EL threshold of the DHDMPV EL device is 6 V at RT and increases to 9V at 77K. Similarly, the EL threshold of the equivalent blend EL device is 7 V at RT and increases to 11V at 77K. This increase in the EL threshold with increasing temperature is in agreement with the known effect of temperature on tunneling injection probability. We may expect a higher threshold of EL at lower temperature, which is in agreement with our experimental results. The experimental result showing a larger EL threshold difference (3V)

between the blend and the DHDMPPV EL devices at 77 K suggests that the charge carriers have been injected into CNMBC in the blend by tunneling. It was found that the current in the injection region dropped by a factor of ten for DHDMPPV and about twenty for the blend on lowering the temperature from RT to 77K. The current decrease in the injection region for both DHDMPPV and the blend at low temperature is due to the lower mobility of charge carriers at low temperature.

The EL intensity as a function of current for the blend EL device increases much more rapidly than for the DHDMPPV EL device at 77 K. The injection current of the blend EL device is much larger than that of the DHDMPPV EL device for the same EL intensity at 77 K, and is also much larger at RT. The lower current and its stronger dependence on EL intensity of the blend EL device compared with the DHDMPPV EL device at 77K suggests that there is more efficient confinement of injected charge carriers and a stronger recombination probability of injected holes in the valence band from the anode and electrons in the conduction band from the cathode in DHDMPPV by CNMBC blending at low temperature.

At both RT and 77 K, we can conclude that DHDMPPV blended with CNMBC exhibits enhanced confinement and an increase in the recombination probability of injected holes and electrons. The EL quantum efficiency and brightness of DHDMPPV were substantially improved by CNMBC blending, while the other EL characteristics were the same. To explain the confinement of injected holes and electrons and the improvement of EL quantum efficiency of DHDMPPV by CNMBC blending, we assume that phase domains of DHDMPPV and CNMBC are randomly

distributed in a two phase structure. Injected holes and electrons can readily move to the DHDMPPV phase domains from the CNMBC domains by hopping under the applied electrical field. However injected holes and electrons cannot easily move back to CNMBC domains from DHDMPPV domains by tunneling in the blend under the applied electrical field because of a potential barrier between the CNMBC and DHDMPPV domains. This implies that the DHDMPPV domain act as an energy trap in the blend confining injected holes and electrons and thereby obtaining a higher recombination probability. Some injected holes and electrons trapped in the energy well of the DHDMPPV domains will escape to CNMBC domains under the influence of the applied electrical field but these carriers will encounter further traps in neighboring DHDMPPV domains and will be repeatedly confined with further opportunities for recombination. Thus the useful injection current is increased, and the non radiative producing current is decreased by the repeated confinement in the DHDMPPV domains in the blend.

We believe that blending is a major advance for improvement of EL quantum efficiency and can be exploited in a variety of different material combinations and device architectures.

## COMPLETED PROJECT SUMMARY

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## SENIOR RESEARCH PERSONNEL:

Dr. L. Akcelrud

Dr. B. Hu

Dr. Z. Yang

Dr. N. Zhang

## JUNIOR RESEARCH PERSONNEL:

Howard Bowman

Ronald Gurge

## PUBLICATIONS (Partially or fully supported by this grant)

1. J. Polym. Sci.: Part A: Polym. Chem., 33, 525-531 (1995) (with R.O. Garay, B. Mayer and R.W. Lenz) "Synthesis and Characterization of Poly[2,5-bis(triethoxy)-1,4-phenylene vinylene]".
2. Synthetic Metals, 71, 2187-2188 (1995) (with M. Aguiar and L. Akcelrud) "Electroluminescent Devices Based on Modified Polystyrene I. Pendant Stilbenyl Groups as Light Emitters".
3. Synthetic Metals, 71, 2189-2190 (1995) (with M. Aguiar and L. Akcelrud) "Electroluminescent Devices Based on Modified Polystyrene II. Pendant Anthracenyl Groups as Light Emitters".
4. J. Macromol. Sci.: Part A: 32, 905-923 (1995) (with R. Garay and R.W. Lenz) "Synthesis and Properties of Phenyl-Substituted Arylene Vinylene Polymers and Copolymers".
5. Macromolecules, 28, 4598-4602 (1995) (with M. Aguiar and L. Akcelrud) "Light-Emitting Polymers with Pendant Chromophoric Groups. I. Poly(stilbenyl-*p*-methoxystyrene)".
6. Macromolecules, 28, 6151-6154 (1995) (with Z. Yang and B. Hu) "Polymer Electroluminescence Using ac or Reverse dc Biasing".
7. Synthetic Metals, 74, 197-199 (1995) (with D. Gonçalves, A. Waddon and L. Akcelrud) "Conducting Blends of Soluble Polyurethane and Poly (*o*-methoxyaniline)".
8. Macromolecules, 29, 4287-4292 (1996) (with R.M. Gurge, A. Sarker, P.M. Lahti and B. Hu) "Red Light Emitting "Push-Pull" Disubstituted Poly(1,4-phenylenevinylenes)".
9. Macromolecules, 29, 3161-3166 (1996) (with M. Aguiar, B. Hu and L. Akcelrud) "Light-Emitting Polymers with Pendant Chromophoric Groups. 2. Poly[styrene-*co*-(*p*-(stilbenylmethoxy)styrene)].

In Press:

10. "Electroluminescence Enhancement from the Confinement of Injected Holes and Electrons by Polymer Blending", with B. Hu and Z. Yang, (Macromolecules).

11. "The Effects of PPV(Poly(*p*-phenylenevinylene) as a Hole Transport Material on Polymer Electroluminescence", with Z. Yang and B. Hu, (Polymer)
12. "Bright Red Electroluminescence from a Blend Plus Multilayer LED with a Balanced and Efficiently Confined Double Injection", with N. Zhang and B. Hu, (Macromolecules).
13. "Efficient Orange Electroluminescence from a Novel Cyano-Substituted, *p*-Phenylenevinylene-Based Copolymer", with N. Zhang and B. Hu, (Macromolecules).