

We have shown that the photoluminescence from silicon-rich silica films is the result of two separate luminescence mechanisms: defect luminescence, possibly from non-bridging oxygen centres or related oxygen vacancies, and radiative recombination of confined excitons. Our results are in broad agreement with those of Shimizu-Iwayama, Komoda and Fischer *et al.*

We have demonstrated electroluminescence from a simple SiO_x based device and have measured its spectrum and current-voltage characteristics. These are very much preliminary results and we are currently working on improving the efficiency of visible emission from such devices by optimising structure and introducing rare-earth dopants.

We have demonstrated that it is possible to access the excited states of rare-earth ions within silicon-rich silica via the absorption of the silicon clusters [24,25]. Recent results published by Polman's group on erbium-doped amorphous silicon have confirmed this [26]. This may open up the possibility of obtaining efficient, narrow-band visible emission from rare-earth doped silicon-rich silica films by careful choice of rare-earth dopant. We are in the process of investigating this further and will publish our results soon.

ACKNOWLEDGEMENTS

We wish to thank the Engineering and Physical Sciences Research Council of the United Kingdom for supporting this work.

REFERENCES

- [1] L.T. Canham, *Appl. Phys. Lett.* **57**, p1046 (1990).
- [2] J.C. Vial, S. Billat, A. Besev, G. Fishman, F. Gaspard, R. Herino, M. Ligeon, F. Madeore, I. Mihalcescu, F. Muller and R. Romestain, *Physica B* **185**, p593 (1993).
- [3] A. Loni, A. J. Simmons, T. I. Cox, P. D. J. Calcott, L.T. Canham, *Electron. Lett.* **31**, p1288 (1995).
- [4] A. Besev, J.C. Vial, F. Gaspard, R. Herino, M. Ligeon, R. Romestain, *Semiconductor-Silicon* 1994 Ed. H.R. Huff, W. Bergholz, K. Sumino, p475 (1994)
- [5] M. Lannoo, C. Delerue, G. Allan and E. Martin (*Mater. Res. Soc. Proc.* **358**, Boston, MA 1994) p13-p24
- [6] B. Delley and E.F. Steigmeier, *Appl. Phys. Lett.* **67**, p2370 (1995)
- [7] P.M. Dertel, T.C. Choy and A.M. Stoneham, *J. Phys. Condens. Matter* **7**, p2507 (1995)
- [8] J. Penczek, A. Knoesen, H.W.H. Lee and R.L. Smith (*Mater. Res. Soc. Proc.* **358**, Boston, MA 1994) p641
- [9] A. Loni, A.J. Simmons, T.I. Cox, P.D.J. Calcott and L.T. Canham, *Elect. Lett.* **31**, p1288 (1995)
- [10] W. Lang, P. Steiner, F. Kozlowski and H. Sandmeier, *J. Luminesc.* **57**, p169 (1993)
- [11] T. Ito and A. Hiraki, *J. Luminesc.* **57**, p331 (1993)
- [12] I.M. Chang, S.C. Pan and Y.F. Chen, *Phys. Rev. B* **48**, p8747 (1993)
- [13] D.J. DiMaria, J.R. Kirtley, E.J. Pakulis, D.W. Dong, T.S. Kuan, F.L. Pesavento, T.N. Theis, J.A. Cutro and S.D. Brorson, *J. Appl. Phys.* **56**, p401 (1984)
- [14] T. Komoda, J.P. Kelly, A. Nejim, K.P. Homewood, P.L.F. Hemment and B.J. Sealy, *Mat. Res. Symp. Proc.* **358**, p163 (1995)
- [15] T. Shimizu-Iwayama, K. Fujita, S. Nakao, K. Saitoh, T. Fujita and N. Itoh, *J. Appl. Phys.* **75**, p7779 (1994)
- [16] G. S. Tompa, D.C. Morton, B. S. Sywe, Y. Lu, E. W. Forsythe, J. A. Ott, D. Smith, J. Khurgin, and B.A. Khan, (*Mater. Res. Soc. Proc.* **358**, Boston, MA 1994) p701-p706
- [17] G. G. Qin, A. P. Li, B. R. Zhang, and B. C. Li, *J. Appl. Phys.* **78** (3), p2006 (1995)
- [18] M. I. Veksler, I. V. Grekhov, S.A. Solov'ev, A. G. Tkachenko, and A. F. Shuleikin, *Tech. Phys. Lett.* **21** (7), p530 (1995)
- [19] A.J. Kenyon, P.F. Trwoga, C. Pitt and G. Rehm, *J. Appl. Phys.* *in press*.
- [20] T. Fischer, T. Muschik, R. Schwarz, D. Kovalev and F. Koch (*Mater. Res. Soc. Proc.* **358**, Boston, MA 1994), p851-p856
- [21] M.A. Stevens Kalceff and M.R. Phillips, *Phys. Rev. B*, **52**, p3122, (1995)
- [22] S. Muneke, T. Yamamaka, Y. Shimogauchi, R. Tohmon, Y. Ohki, K. Nagasawa and Y. Hama, *J. Appl. Phys.* **68**, p1212 (1990)
- [23] H. Koyama, *J. Appl. Phys.* **51**, p2228 (1980)
- [24] A.J. Kenyon, P.F. Trwoga, M. Federighi and C.W. Pitt, *J. Phys. Condens. Matter* **6**, p319, (1994)
- [25] A.J. Kenyon, P.F. Trwoga, M. Federighi and C.W. Pitt (*Mater. Res. Soc. Proc.* **358**, Boston, MA 1994) p117-p122
- [26] J.H. Shin, R. Serna, G.N. van den Hoven, A. Polman, W.G.J.H.M. van Sark and A.M. Vredenberg, *Appl. Phys. Lett.* **68**, p997, (1996)

C.C. Wu¹, J.C. Sturm¹, R.A. Register¹, L. Suponeva² and M.E. Thompson²
¹Advanced Technology Center for Photonic and Optoelectronic Materials (ATC/POEM)
Princeton University, NJ 08544

²Department of Chemistry, University of Southern California, Los Angeles, CA 90089

ABSTRACT

In this paper, we discuss the effects of electron injection on electroluminescence (EL) efficiency in single-layer EL devices using blends of poly(N-vinylcarbazole) (PVK) and poly(3-butyl-p-pyridyl vinylene) (Bu-PPyV). Pure Bu-PPyV thin films suffer from formation of exciton due to the strong interchain interaction. Diluting Bu-PPyV with the high-energy-gap and hole-transporting polymer PVK suppresses exciton formation and substantially raises both photoluminescence (PL) and EL efficiencies. The emission color is converted from red to green indicating a transition from exciton emission to monomer emission of Bu-PPyV. The electron injection and EL efficiency can be further improved by adding small-molecule oxadiazoles into blends as electron-transport materials. In optimized devices, an external EL quantum efficiency (backside emission only) as high as 0.8% photon/electron and practical brightnesses of 100 cd/m² and 1000 cd/m² can be achieved at ~9V and ~13.5V, respectively.

INTRODUCTION

The performance of polymer LEDs is limited by several basic concerns. First, an efficient luminescent polymer does not necessarily have both good hole and electron injection and transport abilities. Also, due to self-quenching or interchain interaction, the luminescence efficiencies of these polymers in solid thin films are usually lower than those in dilute solution [1]. To overcome the carrier transport problems, various approaches have been adopted including the use of low work function metal electrodes [2] and the incorporation of carrier transport layers to form a multilayer structure [3]. Making devices with several spin-coated polymer layers is not always possible because the solvent carrying the second layer might dissolve the layer already deposited. An alternative strategy is to blend together all carrier transport emissive materials in a solvent and then deposit them in a single step [4,5,6]. It has also been reported that diluting a luminescent polymer with another inert high energy gap polymer can reduce the interaction between chromophores and increase the photoluminescence efficiency of the luminescent polymer [1]. In this work, we studied the effects on the optical properties of a device performance of blending the luminescent polymer Bu-PPyV with the high-energy-gap hole-transporting polymer PVK and electron-transporting oxadiazoles.

EXPERIMENTAL

The chemical structures of materials used in this study are shown in Fig. 1. Bu-PPyV was synthesized by cross-coupling the corresponding 2,5-dibromopyridine and E-1-bis(tributylstannylethylene in the presence of a palladium catalyst, as described elsewhere [7,8,9,10]. As a result of the butyl side group, Bu-PPyV is soluble in its conjugated form conventional organic solvents. Two oxadiazoles used are 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD) and 2,5-bis(4-naphthyl)-1,3,4-oxadiazole (BND). Solutions containing

different amounts of Bu-PPyV, PVK and oxadiazoles in chloroform were prepared to give PVK:Bu-PPyV or PVK:oxadiazole: Bu-PPyV blends of different ratios. The blend thin films were then spin-coated onto quartz slides for optical measurements and onto ITO coated glass substrates for device fabrication. Devices were finished by thermally evaporating top metal contacts in a vacuum of 10^{-6} torr through shadow masks to form an array of 2mm by 2mm devices. Metal alloys, such as Mg:Ag, Mg:In and Li:Al alloys were deposited by co-evaporation from two separate sources. All processing and device characterization was carried out under dry nitrogen atmosphere in a glove box. Absorption and photoluminescence spectra of thin films were measured on an AVIV 14DS spectrophotometer and a Perkin-Elmer LS50 luminescence spectrometer, respectively. The EL spectra were recorded by an EG&G monochromator connected to an Electrim CCD camera.

RESULTS AND DISCUSSION

Fig. 2 shows the absorption spectra of Bu-PPyV, PVK and PBD. It is clear that both PVK and PBD have shorter absorption onset wavelengths than Bu-PPyV and therefore higher energy gaps. The absorption spectra of the blends, which are not shown in Fig. 2, are simply weighted superpositions of the spectra of the individual components. The PL spectra of PVK:Bu-PPyV blends with different Bu-PPyV contents are shown in Fig. 3, using an excitation wavelength of 420 nm. This wavelength is used because it is close to the absorption peak of Bu-PPyV and below the absorption onset energy of PVK and PBD. In this way, only Bu-PPyV chromophores are excited. In blends with low Bu-PPyV content, a strong green PL is observed. With the Bu-PPyV content increased above several percent, the PL spectra gradually become broadened and shift to red. By normalizing the integrated PL intensity by the absorption of the same blend film at 420 nm, the relative PL efficiencies of Bu-PPyV chromophores diluted in PVK or PVK:PBD are obtained and displayed in Fig. 4. The efficient green PL in dilute Bu-PPyV blends is the emission of isolated Bu-PPyV chromophores, i.e. Bu-PPyV monomer emission, and the weak red PL in concentrated Bu-PPyV blends and pure Bu-PPyV thin films is from excimer emission due to the strong interchain interaction of Bu-PPyV. The PL efficiency starts dropping rapidly above about 2 wt% Bu-PPyV. It is clear that diluting Bu-PPyV with the high energy gap materials eliminates the interaction between Bu-PPyV chromophores and enhances the PL efficiency of Bu-PPyV chromophores. Similar effects are also observed in THF solutions of Bu-PPyV [10]. Transmission electron microscopy of I₂-stained blend films floated off the substrate reveals no phase separation between the Bu-PPyV and PVK in the as-spun films, consistent with the PL data.

Fig. 5 shows the EL spectra of PVK:Bu-PPyV blends. Pure PVK emits purple light. With extremely low additions of Bu-PPyV, even 0.1 wt%, there is a transition in the EL spectrum from emission characteristics of PVK to emission characteristics of the isolated Bu-PPyV units. Further increase of the Bu-PPyV content above several percent leads to a red-shift of the EL, as observed in PL. The dependence of the EL external quantum efficiency on the content of Bu-PPyV in PVK:Bu-PPyV blends is shown in Fig. 6. The EL efficiency first increases with the Bu-PPyV content and peaks around 1 wt% with an efficiency of $\sim 0.3\%$ photon/electron. The efficiency then drops with further addition of Bu-PPyV. From the results of Fig. 4 and Fig. 6, it is clear that at low concentration, the Bu-PPyV units function as efficient emission centers, and therefore the EL efficiency first rises with the density of Bu-PPyV in the blends and peaks at about 10 times the efficiency of pure PVK. At higher concentrations, due to the interaction of Bu-PPyV chromophores, their luminescence efficiency drops rapidly as seen in Fig. 4, leading to a drop in EL efficiency as well.

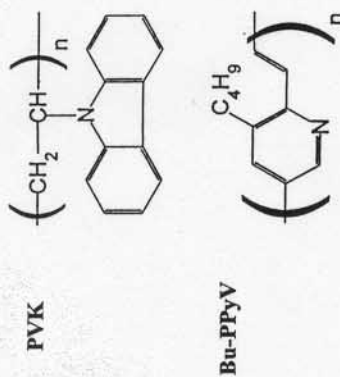


Fig. 1 Chemical structures of PVK, Bu-PPyV, PBD and BND.

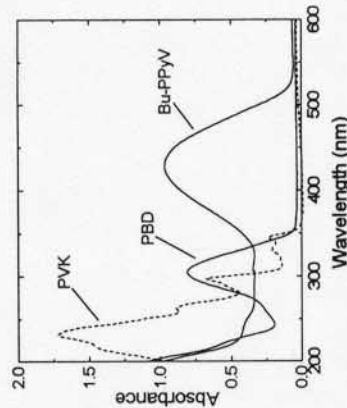


Fig. 2 Absorption spectra of PVK, PBD and Bu-PPyV.

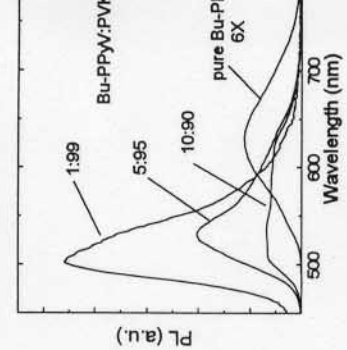


Fig. 3 PL spectra of PVK:Bu-PPyV thin films, excitation wavelength 420 nm.

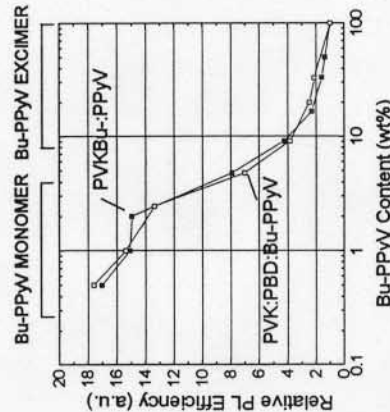


Fig. 4 relative PL efficiency of Bu-PPyV chromophores in blend thin films.

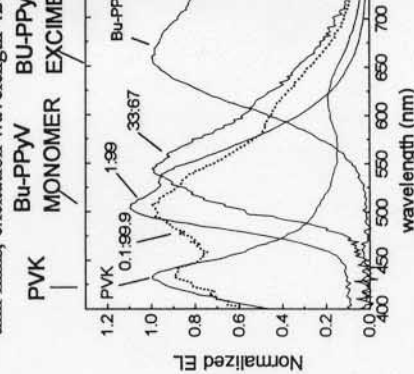


Fig. 5 EL spectra of PVK:Bu-PPyV devices

The effect on EL efficiency of adding electron-transporting molecules PBD to the PVK:Bu-PPyV blend is also shown in Fig. 6. A similar dependence of EL efficiency on Bu-PPyV content is also observed, but PBD can enhance the efficiency severalfold. As shown in Fig. 7, the EL efficiency first increases with added PBD. The highest external EL efficiency 0.8% is achieved with a PVK to PBD ratio of about 100:50 (by weight). Adding more PBD than this actually reduces the EL efficiency. The addition of PBD also has a tremendous effect on the I-V characteristics of the devices, as shown in Fig. 8. All the devices have similar film thicknesses. The rise of forward current with voltage first gets sharper with increasing PBD addition, leading to a reduction in the operating voltage of the devices. However, increasing the PBD:PVK ratio beyond 50:100 does not enhance the current further. Instead, the I-V curve is bent down again, as in the case of the EL efficiency. The current vs. voltage and brightness vs. voltage curves of the optimal blend device with PVK:PBD:Bu-PPyV ratios of 100:50:0.8 are shown in Fig. 9 and 10. These values correspond to an external EL quantum efficiency of 0.8% photon/electron. A practical brightness of 100 cd/m² is achieved at ~12V and 1000 cd/m² at ~16V.

We have also made blend devices using another oxadiazole, BND. It has been reported that BND has a much higher electron mobility than PBD when dispersed in a polymer binder [11]. The comparison of the EL efficiencies of BND and PBD devices is made in Fig. 7. Though the optimal EL efficiency is about the same for both PBD and BND devices, the optimization of BND devices actually occurs at a lower oxadiazole content than for PBD. Also, the optimal BND devices require lower operating voltages than PBD devices, as shown in Figs. 9 and 10. With the optimal BND devices, 100 cd/m² can be achieved at ~9V and 1000 cd/m² at ~13.5V.

Most of the device data presented so far are from devices with Mg:Ag alloy as the metal contact. We have also tried other metals and alloys. The dependence of EL efficiency on metal used is shown in Table 1. We found Mg:In alloy, Li:Al alloy and Ca gave similar EL efficiency as Mg:Ag. For Al, there is a big difference in efficiency between devices with or without oxadiazole additives. Without oxadiazole, the EL efficiency of Al devices is at least one order of magnitude lower than that of Mg:Ag devices. With oxadiazoles, the EL efficiency of Al devices is just two to three times smaller than Mg:Ag devices. It seems that with oxadiazoles, the electron injection is much easier and the metal contact is not so critical. For PVK, the electron injection is much more difficult and the metal contact is critical.

Table 1. Effects of metals on EL efficiency

Mg:Ag	Mg:In	Al	Li:Al	Li:Al	Ca
10:1	10:1		2.5:100	5:100	
PVK:PBD:PPyV 100 : 100 : 5	0.4%	0.2%	0.45%	0.35%	0.4%
PVK:PPyV 100 : 2	0.1%	0.01%			

In all optimal two-component or three-component blend devices, the emission is from the small amount of isolated Bu-PPyV chromophores and is much more efficient than that of pure PVK or PVK/oxadiazole devices. To understand the mechanisms for the emission from these efficient emission centers, we have estimated the energy levels of all materials by electrochemical spectroscopy and electronic absorption spectra [12,13]. The estimated LUMOs for Bu-PPyV, PVK, PBD and BND are -2.9 eV, -2.25 eV, -2.35 eV and -2.16 eV, respectively. The estimated HOMOs for Bu-PPyV, PVK, PBD and BND are -5.4 eV, -5.75 eV, -6.0 eV and -5.6 eV, respectively. Comparing the energy levels suggests at least two possible mechanisms for emission from Bu-PPyV chromophores, i.e. the carrier trapping mechanism and the energy transfer

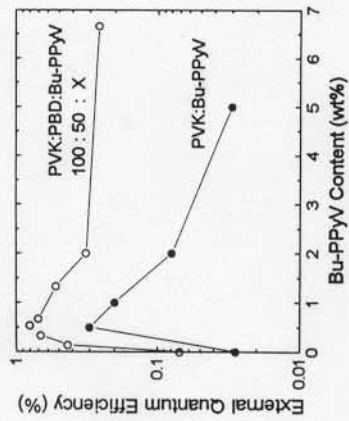


Fig. 6 dependence of EL efficiency on Bu-PPyV content (ITO/blend/Mg:Ag)

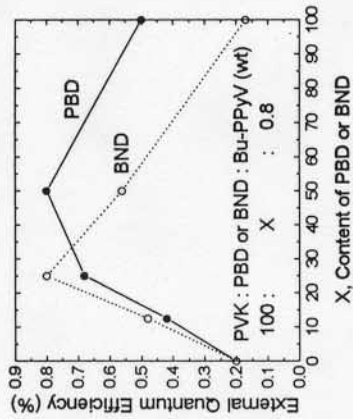


Fig. 7 dependence of EL efficiency on content of PBD or BND (ITO/blend/Mg:Ag)

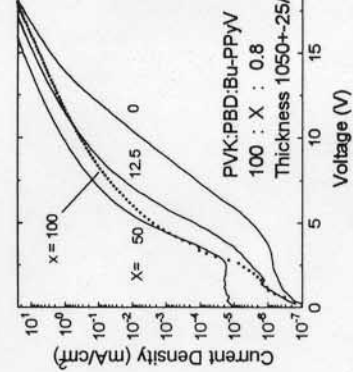


Fig. 8 effects of PBD content on forward characteristics of ITO/blend/Mg:Ag

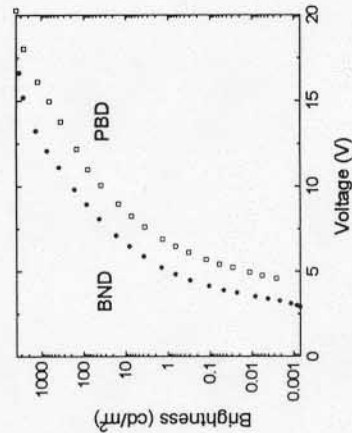


Fig. 9 brightness vs. voltage curves for optimal ITO/blend/Mg:Ag devices

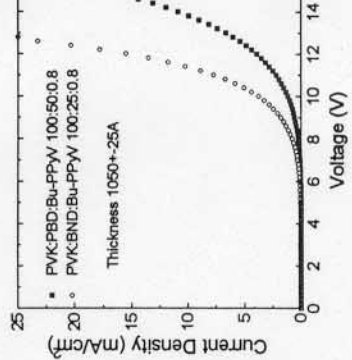


Fig. 10 forward I-V curves for optimal ITO/blend/Mg:Ag devices

mechanism [14]. In the first case, they trap both holes and electrons and form excitons on themselves. In the latter case, they trap excitons formed on carrier transporters.

If one believes that the optimization of the EL efficiency with oxadiazole content is due to better balance of hole and electron currents, the reduction of EL efficiency beyond the optimal oxadiazole content can be explained by the dominance of electron current. That the optimal content of BND is lower than that of PBD can be explained by its better electron transport/injection ability. Also, the sharper rise of the I-V curves in the optimal devices can be related to some hole-electron recombination mechanism. When either hole or electron current is dominant, the balance of both currents and therefore the hole-electron recombination is worse, leading to a higher operating voltage and lower EL efficiency. To support these hypotheses, more experiments and device modeling, taking into account other factors such as space charge effects, are necessary.

CONCLUSIONS

We have presented the results from EL devices made from Bu-PPyV blended with the hole-transporting polymer PVK and the electron-transporting oxadiazole molecules. Diluting Bu-PPyV with the high-energy-gap PVK in thin films reduces the interaction of Bu-PPyV chromophores and enhances both PL and EL efficiency. Adding oxadiazoles into the PVK:Bu-PPyV blend further improves the EL efficiency and reduces the operating voltage. The oxadiazole BND is found to give better devices than PBD, requiring lower operating voltages and smaller oxadiazole additions.

ACKNOWLEDGEMENTS

The authors would like to thank POEM for the support of this work.

REFERENCES

1. S.A. Jenekhe and J.A. Osahemi, *Science* **265**, 765 (1994)
2. D. Braun, A. J. Heeger, *Appl. Phys. Lett.* **58**, 1982 (1991)
3. A.R. Brown, D.D.C. Bradley, P.L. Burn, J.H. Burroughes, R.H. Friend, N. Greenham, A.B. Holmes, and A. Kraft, *Appl. Phys. Lett.* **61**, 2793 (1992)
4. J. Kido, M. Kohda, K. Okuyama and K. Nagai, *Appl. Phys. Lett.* **61** (7), 761 (1992)
5. C. Zhang, S. Hoyer, K. Pakbaz, F. Wudl, and A.J. Heeger, *J. Electron. Mater.* **23**, 453 (1994)
6. G. E. Johnson, K.M. McGrane and M. Stolk, *Pure & Appl. Chem.* **67**, 175 (1995)
7. M.J. Marsella, T.M. Swager, *Polymer Preprints* **33** (1), 1196 (1992)
8. J. Tian, M.E. Thompson, C.C. Wu, J.C. Sturm, R.A. Register, M.J. Marsella, T.M. Swager, *Polymer Preprints* **35** (2), 761 (1994)
9. J. Tian, C.C. Wu, M.E. Thompson, J.C. Sturm, R.A. Register, *Adv. Mater.* **7**, 395 (1995)
10. J. Tian, C.C. Wu, M.E. Thompson, J.C. Sturm, R.A. Register, *Chem. Mater.* **7**, 2190 (1995)
11. H. Tokuhisa, M. Era, T. Tsutsui, and S. Saito, *Appl. Phys. Lett.* **66**, 3433 (1995)
12. M.R. Anderson, M. Berggen, O. Inganäs, G. Gustafsson, J.C. Gustafsson-Carlberg, D. Selse, T. Hjertberg and O. Wennerstrom, *Macromolecules* **28**, 7525 (1995)
13. J. Pommerchne, H. Vestweber, W. Guss, R.F. Mahrt, H. Bässler, M. Porsch and J. Daub, *Adv. Mater.* **7**, 551 (1995)
14. J. Kido, H. Shionoya and K. Nagai, *Appl. Phys. Lett.* **66** (16), 2281 (1995)

Poly(bithiazole)s: A New Class of Conjugated Polymers for Polymer-Based Light-Emitting Diodes

J. K. POLITIS*, J. NANOS*, YI HE**, J. KANICKI***, M.D. CURTIS*

*Department of Chemistry and the Macromolecular Science and Engineering Center, University of Michigan, Ann Arbor, Mi 48109-1055

**Department of Applied Physics, University of Michigan, Ann Arbor, Mi 48109

***Department of Electrical Engineering and Computer Science, University of Michigan, Ann Arbor, Mi 48109-2108

ABSTRACT

A new class of conjugated polymers have been synthesized based on the bithiazole moiety. The photoluminescence (PL) of these polymers ranges throughout the visible from blue-green to red. These materials also show high stability, both thermal and oxidative. Therefore, it appears that this class of polymers are good candidates for polymer-based light emitting diodes.

INTRODUCTION

Over the last decade, conducting polymers have come to the forefront of polymer science. This is due in large part to their potential applications in electroactive devices and LEDs, the most widely studied has been polymer-based light-emitting diodes (LEDs).

There has been much progress since the first crude device, characterized by low efficiency, was reported by the Cambridge group.¹ The most significant improvement in the introduction of either an electron transport/hole blocking layer,^{2,4} a hole transport/electron blocking layer^{5,6} or both.⁷ These multilayer devices have shown improved efficiencies up to 40 times better than the simple three layer device.³ Also, effects of the polymer-metal interface has been greatly reduced. In the simple three layer devices, changing from a high work function metal, aluminum, to a low work function metal, calcium, increases the luminescence efficiency by a factor of 50. In the more complex device, these changes are less dramatic, only a factor of 17.⁸

This improvement, however, focuses on the workings of the device itself. Better electroluminescence efficiency can only be 25% of the photoluminescence efficiency important to also improve the emitting material. Up to now, the two most studied polymers are poly p-phenylene vinylene and polythiophene, along with their derivatives. We have gained some understanding about quantum efficiency from studies on these materials clear that by creating a more amorphous polymer, the electroluminescence efficiency increases. This is evidenced by the fact that as the length of the side chains on these polymers increases, so does the efficiency.^{8,9} Also, in poly(3-alkyl thiophene), the degree of order may be controlled by the polymer regioregularity, and it is observed that intensity of the fluorescence decreases with increasing order.¹⁰ This phenomenon is observed in our first material, poly(5,5'-4,4'-dimonyl-2,2'-bithiazole) (PNBT).¹¹ PNBT exhibits three distinct morphologies: each with differing degrees of crystallinity. Importantly, the fluorescence quenches as the more crystalline phase is obtained. This is presumably due to increased exciplex formation that favor nonradiative decay pathways in the more crystalline phase.

Our laboratory has focused its attention on creating a series of new polymers on the bithiazole moiety. Three materials are currently being studied for their potential LEDs. Using simply one base unit we have created a new class of fluorescent polymer with band gaps ranging from 2-3 eV.