

Conference report

State-of-the-art: in polymer light-emitting diodes
NEOME Polymer LED Mini Symposium
15–17 September 1993, Eindhoven, The Netherlands

David Braun^a, Adam Brown^a, Emiel Staring^a, E.W. Meijer^b

^a*Philips Research Laboratories, Professor Holstlaan 4, 5656 AA Eindhoven, Netherlands*

^b*Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, Netherlands*

Abstract

A symposium focused on recent progress in the field of polymer light-emitting diodes was held in Eindhoven during the period 15–17 September 1993. The following is a brief summary of highlights of the symposium. There will be no published proceedings.

Keywords: Light-emitting diodes; Symposium; Electroluminescence

1. Introduction

The recent discovery that organic semiconducting polymers can function as the active layers in electroluminescent devices [1] has created a new and fascinating area of research [2–45] that extends the scope of organic electroluminescence [46–72]. Advances in polymeric materials make possible new device concepts and a versatile array of display and special lighting applications. With so much interest developing around the world, the NEOME Polymer LED Mini Symposium held in Eindhoven 15–17 September proved a timely forum for sharing recent results.

The scientific program of the conference managed in just 48 h to present a comprehensive view of the state-of-the-art in polymer light-emitting diodes (LEDs). The conference included both synthetic strategies towards a wide variety of potential electroluminescent polymers and examples of device engineering, designed to produce LEDs with a range of visible colors, higher luminescence efficiency and longer lifetimes. In the interest of brevity, this summary emphasizes results not previously available in the literature and does not include the wide assortment of posters. We briefly cover the invited talks. Table 1 lists other oral presentations.

2. Invited talks

Appropriately, the conference began with a presentation by Dr R. Friend from the University of Cambridge, where electroluminescence in conjugated polymers was discovered. Emphasizing the importance of chemistry to this multidisciplinary field, he reported several synthetic advances pioneered by Dr A.B. Holmes. Making good on his promises to “set the ground for the conference” with the history of the field and to relate “recent developments which should point the way to the future”. Dr Friend described tuning emission color, spatial control of the emission region and multilayer device configurations to control carrier injection and capture. The description of numerous developments in their group culminated in the significant announcement that new cyano-PPV derivatives prepared in multilayer structures can achieve 4% efficiency, the highest efficiency reported to date [7]. Because of higher electron affinity, these structures functioned equally well with Al contacts as with the widely used environmentally unstable calcium contacts [1–6].

Continuing in a chemical vein, Dr K. Müllen from the MPI in Mainz explored numerous examples of synthetic progress in the preparation of luminescent oligomers and polymers. The efforts to make blue

luminescent polymers ranged from polymerizing blue emitters such as poly(alkyl anthracene)s and the ladder poly(arylphenylenemethide) to the use of steric hindrance between luminescent species in poly(phenyl perylene-tetra-carboxylic acid amide). The work on ladder polymers highlighted the need for a better understanding of the requirements for an electroluminescent (EL) polymer. Although not guaranteeing a high EL efficiency, a high photoluminescent (PL) efficiency is the only guiding criterion. With the ladder polymers, however, very different PL and EL behavior was observed in the solid state with evidence for excimer creation [73–75].

From an industrial perspective Dr T. Ohnishi of Sumitomo Co. detailed his group's extensive experience with alkoxy-PPV devices. To underscore his blunt assessment of the technical and economic challenges facing the polymer LEDs, Dr Ohnishi presented spectacular IR photos of organic LEDs in operation. These photos dramatically displayed the high device temperatures associated with low efficiency device operation [17, 18].

Being the first to report blue electroluminescence from a polymer, Professor G. Leising from Graz University of Technology emphasized LEDs made from polyphenylene, poly(arylphenylenemethide) and copolymers of the two. He explored how substituents in the ring-opening metathesis changed the luminescence characteristics [31,32].

In reviewing his group's work of recent years, Professor F. Garnier from C.N.R.S. in Paris explored the relationship between physical structure and electrical properties (and, in particular, field-effect mobility) of the chemically pure thiophene oligomers. Work on LEDs using the same materials is only at a very early stage, but the group's accumulated knowledge of the materials

should allow some detailed studies of the physical processes involved in organic LEDs [76–78].

With the aim of understanding the interfaces between metals and polymers, Professor W.R. Salaneck from Linköping University presented a combination of UV and X-ray photoelectron spectroscopy. The spectroscopic work is coupled with quantum chemical calculations performed both at Linköping and in Mons (with Professor J.L. Brédas). They employ model molecules, such as DP7, to allow high quality sample preparation, produce more clearly resolved spectra, and facilitate theoretical interpretation. For PPV, the indications are that Al forms clusters and reacts with the vinylene group to form a covalent bond, Na donates electrons to the PPV to form an ionic bond and Ca behaves similarly to Na. The deposition of metals onto polymer surfaces is performed under UHV conditions. He cautioned that many actual polymers will act otherwise, especially in the presence of oxygen. This is undoubtedly the case with literature-reported high-efficiency polymer LEDs which to date are fabricated under vacuum ($\sim 10^{-6}$ torr) rather than UHV [79–83].

The concluding presentation by Professor A.J. Heeger from Santa Barbara highlighted some of the unique features of plastic LEDs. The impressive view of a mostly plastic LED operating in a bent contortion underscored the mechanical flexibility that polymers allow even in active electronic devices. Switching-speed data of a diode indicated that multiplexing of polymer diode arrays should present few problems. A large part of his talk centered on the careful experimental work of Dr I. Parker, which showed that a tunnel diode model gives an excellent description of the operation of the metal/polymer/metal diodes. After describing the polarized photoluminescence of stretch-oriented poly-

Table 1
Topics of other oral presentations

P. Bäuerle University of Stuttgart	end-capped and alkyl-substituted oligothiophenes [84]
T. Bjørnholm University of Copenhagen	LEDs made from blends of dyes (such as 3-dimethoxy-phenylene-vinylene, bianthracene, DCM and CT) in host polymers (such as polystyrene, PMMA and PVC) [85]
H.J. Byrne MPI in Stuttgart	non-linear luminescence behavior in fullerene crystals [86]
A.P. Davey Trinity College in Dublin	radiative lifetime and quantum yield for <i>trans</i> -aryl ethylylene-type polymers [87]
R.E. Gill University of Groningen	regioregularity of poly(dibutyl-silanylene alkyl-thiophene) copolymers to tune luminescence spectra [44]
F. Louwet Limburg University Diepenbeek	double leaving-group synthetic routes to PPV and poly(<i>p</i> -xylylene) [88]
A. Saxena Los Alamos National Lab	single and multiphonon models of radiative processes in PPV [89]
H. Vestweber University of Marburg	blends with poly(phenyl-PPV), 1,4-distyrylphenyl benzene of DCM in polycarbonate or polystyrene [90]

ethylene blends with MEH-PPV, Professor Heeger challenged the conferees to produce polarized electroluminescence [19–25].

3. Conclusions

The field of polymer LEDs has, since its inception less than four years ago, attracted justified excitement and attention. In that short time many of the fundamental questions as to device operation and material requirements have been well addressed. This conference, the first dedicated to the field, presented a needed opportunity for researchers to present and discuss their data as the field enters a second phase.

In this respect, the conference urged respect for the issues that have not yet been settled satisfactorily. The primary technological concern is long-term device stability. The LEDs are not yet ready for applications that demand 10 000 hours of continuous operation. This issue raises important scientific questions about the nature of device degradation. The inherent stability of the polymers in such devices, and the role of interfaces both metal/polymer and polymer/polymer, would appear to hold some of the answers.

As the conference revealed the multifaceted nature of the field, a general sense of guarded optimism for the future of polymer LEDs arose. Polymer LEDs can produce colors across the visible spectrum. Brightness and efficiency levels are competitive with other material systems. Polymer-processing techniques offer attractive fabrication flexibility and relative ease in large area applications. In addition to electronic and optical properties, polymers can possess unique combinations of chemical and mechanical qualities. Creative mixtures of the above ingredients will present numerous options for new science and technology.

References

- [1] J.H. Burroughes, D.D.C. Bradley, A.R. Brown, R.N. Marks, K. Mackay, R.H. Friend, P.L. Burns and A.B. Holmes, *Nature*, **347** (1990) 539.
- [2] 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** (1992) 2793.
- [3] P.L. Burn, A.B. Holmes, A. Kraft, D.D.C. Bradley, A.R. Brown, R.H. Friend and R.W. Gymer, *Nature*, **356** (1992) 47.
- [4] A.B. Holmes, D.D.C. Bradley, A.R. Brown, P.L. Burn, J.H. Burroughes, R.H. Friend, N.C. Greenham, R.W. Gymer, D.A. Halliday, R.W. Jackson, A. Kraft, J.H.F. Martens, K. Pichler and I.D.W. Samuel, *Synth. Met.*, **55–57** (1993) 4031.
- [5] R.H. Friend, D.D.C. Bradley and A.B. Holmes, *Phys. World*, **5** (1992) 42.
- [6] A.R. Brown, N.C. Greenham, J.H. Burroughes, D.D.C. Bradley, R.H. Friend, P.L. Burn, A. Kraft and A.B. Holmes, *Chem. Phys. Lett.*, **200** (1992) 46.
- [7] N.C. Greenham, S.C. Moratti, D.D.C. Bradley, R.H. Friend and A.B. Holmes, *Nature*, **365** (1993) 628.
- [8] D.D.C. Bradley, A.R. Brown, P.L. Burn, J.H. Burroughes, R.H. Friend, A.B. Holmes, K.D. MacKay and R.N. Marks, *Synth. Met.*, **41–43** (1991) 3135.
- [9] D.D.C. Bradley, A.R. Brown, P.L. Burn, R.H. Friend, A.B. Holmes and A. Kraft, *Proc. International Winter School Electronic Properties of Conjugated Polymers, Kirchberg, Austria, Springer Series on Solid State Sciences*, Vol. 99, Springer, Berlin, 1991.
- [10] P.L. Burn, A.B. Holmes, A. Kraft, D.D.C. Bradley, A.R. Brown and R.H. Friend, *J. Chem. Soc., Chem. Commun.*, (1992) 32.
- [11] L.S. Swanson, J. Shinar, A.R. Brown, D.D.C. Bradley, R.H. Friend, P.L. Burn, A. Kraft and A.B. Holmes, *Phys. Rev. B*, **46** (1992) 15 072.
- [12] P.L. Burn, D.D.C. Bradley, A.R. Brown, R.H. Friend, D.A. Halliday, A.B. Holmes, A. Kraft and J.H.F. Martens, *Proc. International Winter School Electronic Properties of Conjugated Polymers, Kirchberg, Austria, Springer Series on Solid State Sciences*, Vol. 99, Springer, Berlin, 1991.
- [13] A.R. Brown, K. Pichler, N.C. Greenham, D.D.C. Bradley, R.H. Friend and A.B. Holmes, *Chem. Phys. Lett.*, **210** (1993) 61.
- [14] A.R. Brown, K. Pichler, N.C. Greenham, D.D.C. Bradley, R.H. Friend, P.L. Burn and A.B. Holmes, *Synth. Met.*, **55–57** (1993) 4117.
- [15] A.R. Brown, P.L. Burn, D.D.C. Bradley, R.H. Friend, A. Kraft and A.B. Holmes, *Mol. Cryst. Liq. Cryst.*, **216** (1992) 111.
- [16] D.D.C. Bradley, *Adv. Mater.*, **4** (1992) 756.
- [17] T. Nakano, S. Doi, T. Noguchi, T. Ohnishi and Y. Iyechika, *Eur. Patent Applic. No. 91 301 416.3* (1991).
- [18] S. Doi, M. Kuwabara, T. Noguchi and T. Ohnishi, *Synth. Met.*, **55–57** (1993) 4274.
- [19] G. Gustafsson, Y. Cao, G.M. Treacy, F. Klavetter, N. Colaneri and A.J. Heeger, *Nature*, **357** (1992) 477.
- [20] D. Braun, A.J. Heeger and H. Kroemer, *J. Electron. Mater.*, **20** (1991) 945.
- [21] S. Aratani, C. Zhang, K. Pakbaz, S. Höger, F. Wudl and A.J. Heeger, *J. Electron. Mater.*, **22** (1993) 745.
- [22] C. Zhang, H. von Seggern, K. Pakbaz, B. Kraabel, H.-W. Schmidt and A.J. Heeger, *Polym. Prepr.*, **34** (1993) 817.
- [23] H. von Seggern, P. Schmidt-Winkel, C. Zhang, K. Pakbaz, B. Kraabel, A.J. Heeger and H.-W. Schmidt, *Polym. Prepr.*, **34** (1993) 532.
- [24] I.D. Parker, *J. Appl. Phys.*, **75** (1994) 1656.
- [25] D. Braun, D. Moses, C. Zhang and A.J. Heeger, *Synth. Met.*, **55–57** (1993) 4145.
- [26] D. Braun and A.J. Heeger, *Appl. Phys. Lett.*, **58** (1991) 1982.
- [27] D. Braun, G. Gustafsson, D. McBranch and A.J. Heeger, *J. Appl. Phys.*, **70** (1992) 564.
- [28] D. Braun, D. Moses, C. Zhang and A.J. Heeger, *Appl. Phys. Lett.*, **61** (1992) 3092.
- [29] C. Zhang, D. Braun and A.J. Heeger, *J. Appl. Phys.*, **73** (1993) 5177.
- [30] C. Zhang, S. Höger, K. Pakbaz, F. Wudl and A.J. Heeger, *J. Electron. Mater.*, **22** (1993) 413.
- [31] G. Grem, G. Leditzky, B. Ullrich and G. Leising, *Adv. Mater.*, **4** (1992) 36.
- [32] G. Grem and G. Leising, *Synth. Met.*, **55–57** (1993) 4105.
- [33] Y. Ohmori, M. Uchida, K. Muro and K. Yoshino, *Solid State Commun.*, **80** (1991) 605.
- [34] Y. Ohmori, M. Uchida, K. Muro and K. Yoshino, *Jpn. J. Appl. Phys.*, **30** (1991) L1941.
- [35] Y. Ohmori, C. Morishima, U. Uchida and K. Yoshino, *Jpn. J. Appl. Phys.*, **31** (1992) L568.

- [36] Y. Ohmori, C. Morishima, M. Uchida and K. Yoshino, *Synth. Met.*, 55-57 (1993) 4180.
- [37] M. Uchida, Y. Ohmori, C. Morishima and K. Yoshino, *Synth. Met.*, 55-57 (1993) 4168.
- [38] M. Uchida, Y. Ohmori, T. Noguchi, T. Ohnishi and K. Yoshino, *Jpn. J. Appl. Phys.*, 32 (1993) L921.
- [39] S. Karg, W. Rieß, V. Dyakonov and M. Schwoerer, *Synth. Met.*, 54 (1992) 427.
- [40] S. Karg, W. Rieß, J. Gmeiner and M. Schwoerer, *Synth. Met.*, 55-57 (1993) 4186.
- [41] H. Vestweber, A. Greiner, U. Lemmer, R.F. Fohrt, R. Richert, W. Heitz and H. Bässler, *Adv. Mater.*, 4 (1992) 661.
- [42] Z. Yang, I. Sokolik and F.E. Karasz, *Macromolecules*, 26 (1993) 1188.
- [43] I. Sokolik, Z. Yang, F.E. Karasz and D.C. Morton, *J. Appl. Phys.*, 74 (1993) 3584.
- [44] G.G. Malliaras, J.K. Herrema, J. Wildeman, R.H. Wieringa, R.E. Gill, S.S. Lampoura and G. Hadziioannou, *Adv. Mater.*, 5 (1993) 721.
- [45] H. Suzuki, H. Meyer, J. Simmerer, J. Yang and D. Haarer, *Adv. Mater.*, 5 (1993) 743.
- [46] C.W. Tang, S.A. VanSlyke and C.H. Chen, *J. Appl. Phys.*, 65 (1989) 3610.
- [47] C.W. Tang and S.A. VanSlyke, in S. Shionoya and H. Kobayashi (eds.), *Electroluminescence*, Springer, Berlin, 1989, p. 356.
- [48] C.W. Tang, C.H. Chen and R. Goswami, *US Patent No. 4 769 292* (1988).
- [49] C.W. Tang and S.A. VanSlyke, *Appl. Phys. Lett.*, 51 (1987) 913.
- [50] N. Takada, T. Tsutsui and S. Saito, *Appl. Phys. Lett.*, 63 (1993) 2032.
- [51] T. Tsutsui, E.-I. Aminaka, Y. Fujita, Y. Hamada and S. Saito, *Synth. Met.*, 55-57 (1993) 4157.
- [52] Y. Hamada, C. Adachi, T. Tsutsui and S. Saito, *Jpn. J. Appl. Phys.*, 31 (1992) 1812.
- [53] Y. Hamada, C. Adachi, T. Tsutsui and S. Saito, *Opto-electronics, Dev. Technol.*, 7 (1992) 83.
- [54] M. Era, C. Adachi, T. Tsutsui and S. Saito, *Thin Solid Films*, 210/211 (1992) 468.
- [55] T. Tsutsui, C. Adachi and S. Saito, *Synth. Met.*, 41-43 (1991) 1193.
- [56] C. Adachi, T. Tsutsui, S. Saito, M. Watanabe and M. Koishi, *Chem. Phys. Lett.*, 182 (1991) 143.
- [57] C. Adachi, T. Tsutsui and S. Saito, *Opto-electronics, Dev. Technol.*, 6 (1991) 25.
- [58] M. Era, C. Adachi, T. Tsutsui and S. Saito, *Chem. Phys. Lett.*, 178 (1991) 488.
- [59] C. Adachi, T. Tsutsui and S. Saito, *Proc. Conf. Photochemical Processes in Organized Molecular Systems, Yokohama, Japan, 1991*, p. 437.
- [60] C. Adachi, T. Tsutsui and S. Saito, *Appl. Phys. Lett.*, 57 (1990) 531.
- [61] C. Adachi, T. Tsutsui and S. Saito, *Appl. Phys. Lett.*, 56 (1990) 799.
- [62] C. Adachi, T. Tsutsui and S. Saito, *Appl. Phys. Lett.*, 55 (1989) 1489.
- [63] C. Adachi, S. Tokito, T. Tsutsui and S. Saito, *Jpn. J. Appl. Phys.*, 27 (1988) L713.
- [64] C. Adachi, S. Tokito, T. Tsutsui and S. Saito, *Jpn. J. Appl. Phys.*, 27 (1988) L269.
- [65] C. Hosokawa, H. Higashi and T. Kusumoto, *Appl. Phys. Lett.*, 62 (1993) 3238.
- [66] C. Hosokawa, H. Tokailin, H. Higashi and T. Kusumoto, *Appl. Phys. Lett.*, 63 (1993) 1322.
- [67] C. Hosokawa, H. Tokailin, H. Higashi and T. Kusumoto, *Appl. Phys. Lett.*, 60 (1992) 1220.
- [68] C. Hosokawa, N. Kawasaki, S. Sakamoto and T. Kusumoto, *Appl. Phys. Lett.*, 61 (1992) 2503.
- [69] M. Nohara, M. Hasegawa, C. Hosokawa, H. Tokailin and T. Kusumoto, *Chem. Lett.*, (1990) 189.
- [70] M. Hiramoto, J. Tani and M. Yokoyama, *Appl. Phys. Lett.*, 62 (1993) 666.
- [71] M. Hiramoto, H. Fujiwara and M. Yokoyama, *J. Appl. Phys.*, 72 (1992) 3781.
- [72] J. Littman and P. Martic, *J. Appl. Phys.*, 72 (1993) 1957.
- [73] U. Scherf and K. Müllen, *Makromol. Chem. Rapid Commun.*, 12 (1991) 489.
- [74] M. Baumgarten, U. Anton, L. Gherghel and K. Müllen, *Synth. Met.*, 55-57 (1993) 4807.
- [75] K. Müllen and U. Scherf, *Synth. Met.*, 55-57 (1993) 739.
- [76] F. Garnier, G. Horowitz, X. Peng and D. Fichou, *Adv. Mater.*, 2 (1990) 592.
- [77] G. Horowitz, X.-Z. Peng, D. Fichou and F. Garnier, *Synth. Met.*, 51 (1992) 419.
- [78] F. Garnier, F. Deloffre, G. Horowitz and R. Hajlaoui, *Synth. Met.*, 55-57 (1993) 4747.
- [79] W.R. Salaneck, *Rep. Progr. Phys.*, 54 (1991) 1215.
- [80] P. Dannelun, M. Lögdlund, M. Fahlman, M. Boman, S. Stafström, W.R. Salaneck, R. Lazzaroni, C. Fredriksson, J.L. Brédas, S. Graham, R.H. Friend, A.B. Holmes, R. Zamboni and C. Taliani, *Synth. Met.*, 55-57 (1993) 212.
- [81] C. Fredriksson, R. Lazzaroni, J.L. Brédas, P. Dannelun, M. Lögdlund and W.R. Salaneck, *Synth. Met.*, 55-57 (1993) 4632.
- [82] M. Fahlman, O. Lhost, F. Meyers, J.L. Brédas, S.C. Graham, R.H. Friend, P.L. Burn, A.B. Holmes, K. Kaeriyama, Y. Sonoda, M. Lögdlund, S. Stafström and W.R. Salaneck, *Synth. Met.*, 55-57 (1993) 263.
- [83] M. Lögdlund, W.R. Salaneck, F. Meyers, J.L. Brédas, G.A. Arbuckle, R.H. Friend, A.B. Holmes and G. Froyer, *Macromolecules*, 26 (1993) 3815.
- [84] P. Bäuerle, G. Götz, U. Segelbacher, D. Huttenlocher and M. Mehring, *Synth. Met.*, 55-57 (1993) 4768.
- [85] P. Frederiksen, T. Bjørnholm, H.G. Madsen and K. Bechgaard, *J. Mater. Chem.*, (1994) in press.
- [86] H.J. Byrne, W.K. Master, W.W. Ruhle, A. Mittelbach and S. Roth, *Appl. Phys. A*, 56 (1993) 235.
- [87] H. Winkler, A.P. Davey and W. Blau, *Diplomarbeit Thesis*, University of Regensburg, 1993.
- [88] F. Louwet, D. Vanderzande, P. Adriaenssens, J. Gelan and J. Mullens, *Macromolecules* (1994) submitted for publication.
- [89] F.X. Bronold, A. Saxena and A.R. Bishop, *Phys. Rev. B*, 48 (1993) 13 162.
- [90] H. Vestweber, J. Oberski, A. Greiner, W. Heitz, R.F. Mahrt and H. Bässler, *Adv. Mater. Opt. Electron.*, 2 (1993) 197.