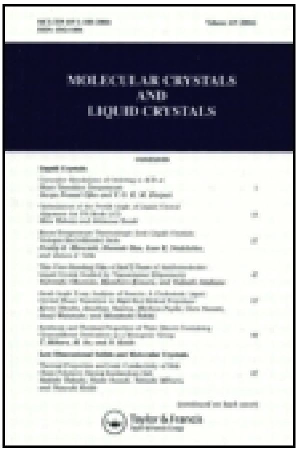


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Electroluminescence with Conjugated Polymers and Oligomers

Wilhelm Graupner [a], Gabriele Grem [a], Farideh Meghdadi [a], Christian Paar [a], Günther Leising [a], Ullrich Scherf [b], Klaus Müllen [b], Walter Fischer [c] & Franz Stelzer [c]

[a] Institut für Festkörperphysik, TU Graz, Austria

[b] Max-Planck-Institut für Polymerforschung, Mainz, Germany

[c] Institut für chemische Technologie organischer Stoffe, TU Graz, Austria

To cite this article: Wilhelm Graupner, Gabriele Grem, Farideh Meghdadi, Christian Paar, Günther Leising, Ullrich Scherf, Klaus Müllen, Walter Fischer & Franz Stelzer (1994): Electroluminescence with Conjugated Polymers and Oligomers, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 256:1, 549-554

To link to this article: http://dx.doi.org/10.1080/10587259408039290

Mol. Cryst. Liq. Cryst. 1994, Vol. 256, pp. 549–554
Reprints available directly from the publisher
Photocopying permitted by license only

ELECTROLUMINESCENCE WITH CONJUGATED POLYMERS AND OLIGOMERS

WILHELM GRAUPNER, GABRIELE GREM, FARIDEH MEGHDADI,
CHRISTIAN PAAR AND GÜNTHER LEISING
Institut für Festkörperphysik, TU Graz, Austria.

ULLRICH SCHERF AND KLAUS MÜLLEN
Max-Planck-Institut für Polymerforschung, Mainz, Germany.

WALTER FISCHER AND FRANZ STELZER
Institut für chemische Technologie organischer Stoffe, TU Graz, Austria.

Abstract We report on the optical properties of polymers and oligomers used in light emitting diodes (LEDs) prepared by solution processing or vacuum deposition. Special emphasis is put on the comparison of PPP and its oligomers to *planarized* forms of PPP.

INTRODUCTION

Conducting polymers - studied since 1977 for their conductivity[1] - have become a primary object of interest for the possible commercial applications of their optical properties in the undoped state[2]. After the pioneering work of Burroughes et al.[3] several factors accelerated the progress in the field of Electroluminescence (EL) of conjugated polymers and oligomers. There is the need for the computer and TV-industry to improve present screen technologies towards larger displays and better pixel resolution[4]. A lot of fundamental work was done on the processibility of conjugated polymers that proved to be very useful for the production of high quality thin films required for LEDs. Processing of metastable, soluble, non-conjugated precursor materials and subsequent in situ thermal conversion is connected to the name of W. J. Feast for polyacetylene[5]. This type of procedure is now being used for a range of materials (poly(*para*-phenylene) (PPP)[6], poly(*para*-phenylenevinylene) (PPV)[2]). Another step towards processibility is the attachment of solubilising flexible sidegroups to the conjugated backbone (e. g. poly(3-alkylthiophenes)[7]). Based on the knowledge about conjugated polymers scientists developed strategies to either choose the colour of the EL by picking a certain polymer (red[8], yellow-green[3], blue:[9-12]) or to tune the bandgap of macromolecules[13]. The interaction between theory and synthetic skills allowed an increase in the efficiency of polymer LEDs by introducing electron-transport/hole-blocking layers[2] or by synthesizing copolymers that form quantum well structures along the polymer chain[14,15]. Finally new theoretical concepts of the metal-polymer junction are being developed[16] to describe the bandstructure within the polymers which should be different from inorganic semiconductors.

EXPERIMENTAL

Device Preparation

A typical device (Fig.1) used for this work utilizes a substrate of an indium tin oxide (ITO) layer coated on glass forming the hole injecting contact. The substrate is covered by an active organic layer either by spin coating (wet process) or vacuum deposition (dry process). Aluminum and calcium contacts, as an electron injection layer with low work functions, were produced by vacuum deposition.

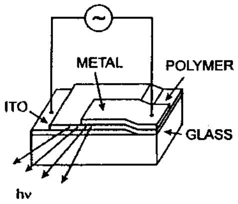


FIGURE 1 Schematic view of a polymer LED.

Active Layers by Spin Coating

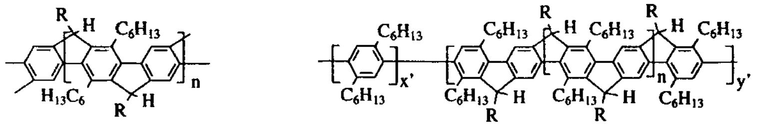


FIGURE 2 Chemical structure of (left) LPPP and (right) CPLPPP.

Figure 2 shows the chemical composition of the two PPP-type ladder polymers that were brought onto the substrate by spin coating. The PPP used was prepared according to Ballard's route[6] by thermal conversion of the spin coated films at temperatures above 300°C. In Figure 2 (left) a PPP-type ladder polymer (LPPP) is shown which owes its sterically planar structure to a bridging of functionalized PPP-precursors[17] where R stands for -1.4-C_6H_4-$C_{10}H_{21}$. A segmented copolymer (CPLPPP) of planarized oligophenyls with

2.5-dialkyl-1.4-phenylene spacers is shown in Figure 2 (right) where x=0.6 and y=0.4[18,15].

Active Layer by Vacuum Deposition

The active layers are made by vacuum deposition of Yamamoto PPP[19] and *para*-hexaphenyl (PHP) from quartz crucibles[20]. We chose PHP for its character as a model compound for PPP and since it is the longest oligophenyl being synthesized in a very pure state[21]. Yamamoto PPP was taken because of our purification procedure it does not contain oligomers shorter than PHP. The thickness of the deposited active layers is around 200-300nm, monitored by a quartz crystal balance. The typical substrate temperature is about 200°C while the source is heated up to 650°C.

Device Characterization

Luminance is measured using a Minolta LS 100 luminance meter. Photoluminescence (PL) and electroluminescence data are obtained in air (Ar atmosphere for Ca-electrodes).

RESULTS AND DISCUSSION

Optical Characterization

In Figures 3-7 the EL, PL and optical absorption spectra (OD) of the active layers in the devices are shown with their peak values normalized to unity. The curves denoted with (a) represent the optical absorption while (b) and (c) correspond to the PL and EL emission respectively.

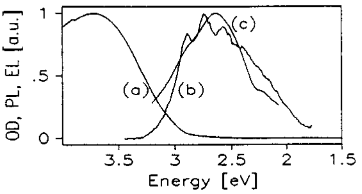
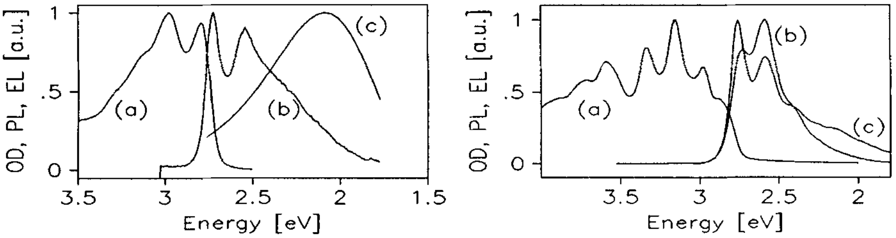


FIGURE 3 OD, EL and PL of precursor PPP.

The energetic position of the absorption peaks (E_a) is used to determine the number of conjugated phenyl rings (n_{ph}) by comparison to oligophenyls. For the LPPP and CPLPPP we use data on *planarized oligophenyls*[22] which yield (1), *conventional* oligophenyls[24] give (2):

$$E_a = \frac{4.56\text{eV}}{n_{ph}^{0.220}} \qquad (1) \qquad\qquad E_a = \left[3.36 + \frac{3.16}{n_{ph}}\right] \text{eV} \qquad (2)$$

It is seen that planarizing PPP decreases the energetic position of the absorption peak of systems with the same number of conjugated phenyl rings by about 0.8eV (Table I).



FIGURES 4/5 OD, EL and PL of (4) LPPP and (5) CPLPPP.

The well resolved vibrational structure in the absorption spectra of LPPP and CPLPPP originates in the suppression of the rotational degree of freedom, which smears out the vibrational splitting[23]. For the two types of PPP we used for LED production - in two different processes - the average conjugation length is about nine phenyl rings. The chain length of the Y-PPP was determined via the luminescence excitation spectrum since the chains are oriented perpendicular to the substrate. This means that the absorption parallel to the chainlength is *not* observed in a transmission measurement with the optical axis perpendicular to the substrate (Figures 6 and 7).

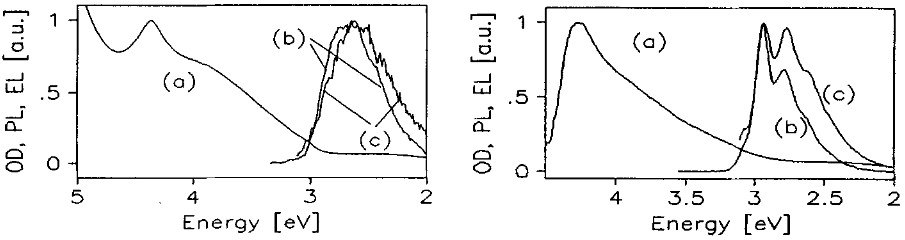


FIGURE 6/7 OD, EL and PL of (6) Y-PPP and (7) PHP.

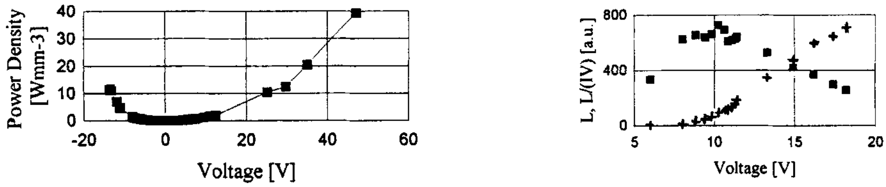
We do also show the *dominant* PL and EL peaks (E_p and E_e respectively) and the difference between the absorption and EL-emission peaks (ΔE) in Table I. It is obvious that PPP systems with a rotational degree of freedom yield a large Stokes shift of around 1 eV between the absorption and the emission peaks. The LPPP and the CPLPPP show only a difference of a few tenths of eV. The red shift by 0.65eV of the EL-peak with respect to the PL in some LPPP-devices[4,23] is the result of a degradation of the polymer under device-operation which we were, so far, not able to prevent. The CPLPPP does not show this behaviour.

TABLE I Physical parameters of LED materials;

Material	n_{ph}	E_a [eV]	E_e [eV]	E_p [eV]	ΔE [eV]
LPPP	9.4	2.79	2.07	2.72	0.72
CPLPPP	8.1	2.88	2.76	2.58	0.12
PPP[6]	8.8	3.72	2.62	2.74	1.10
PPP-Y	8.5	3.73	2.62	2.68	1.11
PHP	6.0	3.89	2.93	2.93	0.96

Device operation

The active layer of a typical device consists of a 6mm^2 pad with a thickness of about 200nm. In Figure 8 we show the electrical power density in a PHP LED assuming a homogeneous conversion of electrical power into light and heat throughout the whole volume of the active layer. This high power density is expected to lead to significant warming of the active layer which can result in a decrease of EL yield.



FIGURES 8/9 PHP LED: (8) power density and (9) $\frac{L}{IV}$ (■), L (+)

We tried to observe this effect by measuring the luminance L and the I-V characteristics of a PHP LED simultaneously. L and the ratio $\frac{L}{IV}$ versus the driving voltage V are shown in Figure 9. The maximum of $\frac{L}{IV}$ at approximately 10V at the onset of the linear L-V relation is in qualitative agreement with what is seen for oligothiophenes[25].

CONCLUSION

The optical properties of PPP-type ladder polymers and copolymers are compared to different types of PPP and *para*-hexaphenyl. Planarization of the PPP-backbone leads to better vibrational resolution in both absorption and emission spectra. The Stokes shift is significantly smaller for the PPP-type ladder polymers compared to systems with a rotational degree of freedom for the phenyl rings. We have also shown that solution processing and vacuum deposition lead to similar results in PL and EL. By vacuum deposition it is however possible to grow oriented oligomer layers.

We gratefully acknowledge the financial support of the Volkswagen Stiftung.

REFERENCES

1. C. K. Chiang, C. R. Fincher, Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, S. C. Gau, A. G. MacDiarmid, Phys. Rev. Lett., 39, 1098 (1977).
2. A. R. Brown, N. C. Greenham, R. W. Gymer, K. Pichler, D. D. C. Bradley, R. H. Friend, P. L. Burn, A. Kraft, A. B. Holmes, NATO ASI Series, 256, 87 (1993).
3. 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, 347, 539 (1990).
4. G. Leising, NATO ASI Series, 256, 117 (1993).
5. J. H. Edwards, W. J. Feast, Polymer Commun., 21, 595 (1980).
6. D. G. H. Ballard, A. Courtis, I. M. Shirley, S. C. Taylor, Macromolecules, 21, 294 (1983).
7. K. Y. Jen, G. G. Miller, R. L. Elsenbaumer, J. Chem. Soc., Chem. Commun., 1346 (1986).
8. V. Ohmori, M. Uchida, K. Muro, K. Yoshino, Japanese Journal of Applied Physics, 30, L 1938 (1991).
9. V. Ohmori, M. Uchida, K. Muro, K. Yoshino, Japanese Journal of Applied Physics, 30, L 1941 (1991).
10. G. Grem, G. Leditzky, B. Ullrich, G. Leising, Advanced Materials, 4, 36 (1992).
11. I. Sokolik, Z Yang., F. E. Karasz, D. C. Morton, J. Appl. Phys., 74, 3584 (1993).
12. C. Zhang, H. von Seggern, K. Pakbaz, B. Kraabel, H. W. Schmidt, A. J. Heeger Synthetic Metals, 62, 35 (1994).
13. F. Meyers, A. J. Heeger, J. L. Bredas, *Synthetic Metals*, 55-57, 4308 (1993).
14. D. D. C. Bradley, A. R. Brown, P. L. Burn, R. H. Friend, A. B. Holmes, A. Kraft, Springer Series in Solid State Sciences, 107, 304 (1992).
15. G. Grem, C. Paar, J. Stampfl, G. Leising, J. Huber, U. Scherf, submitted to Chemistry of Materials
16. S. A. Brazovskii, N. N. Kirova, Synthetic Metals, 55-57, 4385 (1993).
17. U. Scherf, K. Müllen, Makromol. Chem., Rapid Commun., 12, 489 (1991).
18. U. Scherf, K. Müllen, G. Leising and HOECHST AG, Patent 4331401.5.
19. T. Yamamoto, A. Yamamoto, Chemistry Letters, 353 (1977).
20. G. Leising et al., submitted to Advanced Materials.
21. G. Louarn, L. Athouel, G. Froyer, S. Lefrant, Synthetic Metals, 55-57, 4762 (1993).
22. J. Grimme, U. Scherf, K. Müllen, in preparation
23. J. Huber, K. Müllen, J. Salbeck, H. Schenk, U. Scherf, T. Stehlin, R. Stern, submitted to Acta Polym.
24. G. Leising, K. Pichler, F. Stelzer, Springer Series in Solid State Sciences, 91, 100 (1989).
25. F. Geiger, M. Stoldt, H. Schweizer, P. Bäuerle, E. Umbach, Advanced Materials, 5, 922 (1993).