

Electroluminescence and Photoluminescence Efficiency of Poly(*p*-phenylenevinylene) Derivatives

E.G.J. Staring, R.C.J.E. Demandt, D. Braun, G.L.J. Rikken, Y.A.R.R. Kessener,
A.H.J. Venhuizen, M.M.F. van Knippenberg, and M. Bouwmans

Philips Research Laboratories, Prof. Holstlaan 4, 5656 AA Eindhoven, The Netherlands

Abstract

Alkoxy, alkyl, and cyano derivatives of poly(*p*-phenylenevinylene) [PPV] are used as the emissive layers in light-emitting diodes [LEDs] to obtain luminescence from red to blue. We present the luminescence efficiency for these soluble PPV derivatives, comparing the photoluminescence [PL] yields with the electroluminescence [EL] yields. PL efficiency increases with the fraction of non-conjugated units. EL efficiency depends not only on the radiative recombination efficiency of the emitting material but also on carrier transport to and within the material. Efforts to improve the efficiency and long term stability of these polymer LEDs are challenged by efficient and balanced carrier injection.

1. INTRODUCTION

The high EL efficiency observed in red cyano-PPV derivatives with high electron affinities[1] suggests also the cyano-PPV derivatives as candidates for efficient green and blue EL. We report the synthesis, PL efficiency, and EL efficiency of green and blue cyano-PPV derivatives.

2. DEVICE FABRICATION

Figure 1 shows the synthesis of the cyano-PPVs. Devices are prepared on patterned ITO substrates. Polymer layers are spun-cast from toluene or toluene/THF solutions containing 0.5-2.0 % polymer. The first polymer layer is a hole transport layer consisting of dialkyl-PPV which is thermally cross-linked to prevent it from dissolving during spin-casting of the top polymer layer. The cyano-PPV films are spin-cast next. 2500Å Indium contacts are deposited on top by vacuum evaporation at pressures below 2×10^{-6} mbar yielding active device areas of 4 – 81 mm². LEDs made from the alkoxy-PPVs [2] and alkyl-PPVs [3] have Calcium contacts and no hole transport layer. All processing steps are carried out in a nitrogen atmosphere.

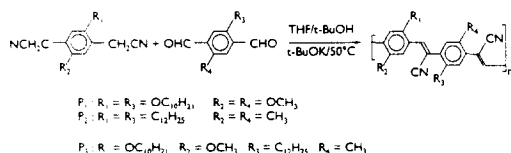


Figure 1. Synthesis of cyano-PPV derivatives.

3. PHOTOLUMINESCENCE SPECTRA

The PL spectra, recorded using a Perkin Elmer LS50 Luminescence Spectrometer, appear in Figure 2. Although poor color purity might be expected from the broad emission bands, the CIE color coordinates (see Figure 3) of the cyano-PPV derivatives compare favorably with the corners of the triangular region desired for a 3-color display. With the present emission spectra, the required color range is almost accessible.

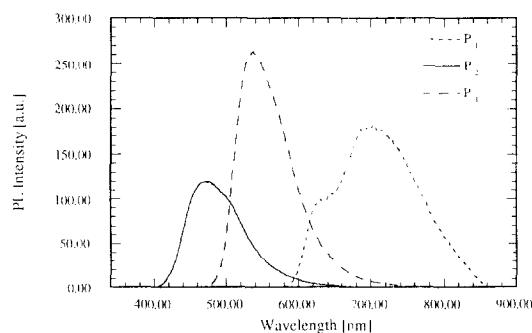


Figure 2. PL Intensity of cyano-PPV derivatives.

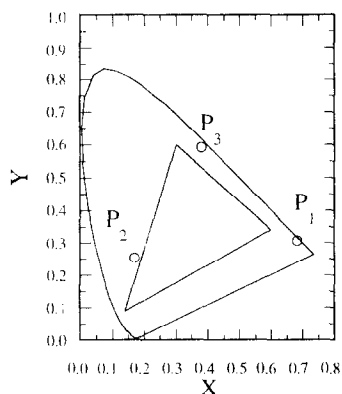


Figure 3. CIE color coordinates of cyano-PPV derivatives.

4. LUMINESCENCE EFFICIENCY

For EL, external quantum efficiencies in photons per electron are measured with a calibrated silicon photo diode. The slightly non-Lambertian geometry of the emission pattern is corrected by comparison to measurements performed in a calibrated integrating sphere.

PL efficiencies are recorded for solid polymer films drop-cast onto glass substrates. The 514 nm and 458 nm lines of an argon ion laser and the 413 nm line of a krypton laser are used as excitation sources. The luminescence is collected with a calibrated integrating sphere, corrected for the spectral dependencies of the luminescence, the collection optics, and reflection at the sample surface.

Table 1
External EL efficiency and PL efficiency of cyano-PPV derivatives

Polymer	EL Efficiency [%]	PL Efficiency [%]
P ₁	0.8	14-20
P ₂	0.005	12-18
P ₃	0.2	26

Tables 1-3 compare the EL and PL efficiencies of the cyano-PPVs to those of alkoxy-PPVs [2] and alkyl-PPVs [3]. The presence of non-conjugated (higher band gap) segments improves PL yield by confining the excitons to the conjugated segments of the chain and preventing the excitons from recombining non-radiatively. Similarly, the non-conjugated segments impede electron and hole transport along the chain and, thereby, impede exciton formation. If the trends observed

in alkoxy-PPV and alkyl-PPVs apply also to cyano-PPVs, partial conjugation to enhance radiative recombination should improve EL efficiency.

Table 2
External EL efficiency and PL efficiency as a function of non-conjugated fraction for dialkoxy-PPV.

Non-Conjugated Fraction [%]	EL Efficiency [%]	PL Efficiency [%]
<5	0.26-0.61	7.8-13
6.5	0.34-0.50	14
8	1.0-1.4	14
15	0.71-0.84	19.6
37.5	0.26-0.31	23.6

Table 3
External EL efficiency and PL efficiency as a function of non-conjugated fraction for dialkyl-PPV.

Non-Conjugated Fraction [%]	EL Efficiency [%]	PL Efficiency [%]
5	0.21	47
15	0.17	55
45	0.07	63

5. CONCLUSION

The wide discrepancy between the PL efficiency and the EL efficiency in these PPV derivatives indicates that optimizing carrier injection, charge transport, radiative efficiency and device geometry can lead to further improvements in device performance.

REFERENCES

1. N.C. Greenham, S.C. Moratti, D.D.C. Bradley, R.H. Friend, and A.B. Holmes, *Nature* 365 (1993) 628.
2. D. Braun, E.G.J. Staring, R.C.J.E. Demandt, G.L.J. Rikken, Y.A.R.R. Kessener, A.H.J. Venhuizen, and M. Bouwmans, *Synth. Met.* 66 (1994) 75.
3. E.G.J. Staring, R.C.J.E. Demandt, D. Braun, G.L.J. Rikken, Y.A.R.R. Kessener, A.H.J. Venhuizen, H. Wynberg, W. ten Hoeve, and K.J. Spoelstra, *Adv. Mater.* submitted (1994).