# Thermal control of near-infrared and visible electroluminescence in alkyl-phenyl substituted polythiophenes

Magnus Berggren, Göran Gustafsson, Olle Inganäs, Mats Andersson, Olof Wennerström and Thomas Hjertberg

# **Linköping University Post Print**

N.B.: When citing this work, cite the original article.

# Original Publication:

Magnus Berggren, Göran Gustafsson, Olle Inganäs, Mats Andersson, Olof Wennerström and Thomas Hjertberg, Thermal control of near-infrared and visible electroluminescence in alkylphenyl substituted polythiophenes, 1994, Applied Physics Letters, (65), 12, 1489-1491. http://dx.doi.org/10.1063/1.112021

Copyright: American Institute of Physics (AIP)

http://www.aip.org/

Postprint available at: Linköping University Electronic Press http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-74938

# Thermal control of near-infrared and visible electroluminescence in alkyl-phenyl substituted polythiophenes

M. Berggren, G. Gustafsson, and O. Inganäs Laboratory of Applied Physics, University of Linköping, S-581 83 Linköping, Sweden

### M. R. Andersson

Department of Organic Chemistry and Department of Polymer Technology, Chalmers University of Technology, S-412 96 Göteborg, Sweden

## O. Wennerström

Department of Organic Chemistry, Chalmers University of Technology, S-412 96 Göteborg, Sweden

# T. Hiertberg

Department of Polymer Technology, Chalmers University of Technology, S-412 96 Göteborg, Sweden

(Received 26 April 1994; accepted for publication 11 July 1994)

We report electroluminescence from a regioregular alkyl-phenyl substituted polythiophene. The polymer film exists in two forms, giving widely different optical absorption, as well as photoluminescence and electroluminescence spectra. In the low-bandgap form, we observe high emission intensity centered at 1.55 eV (800 nm), well into the infrared, while the high-bandgap form gives a maximum at 1.85 eV (670 nm). The conversion from the high-bandgap form to the low-bandgap form can be done by thermal treatment of the polymer light emitting diodes.

Polymeric electroluminescent (EL) devices have attracted considerable interest lately. They exhibit high luminance, high efficiency, and can be driven at a low dc voltage. One of the major advantages of using organic molecules or polymers, as compared to inorganic materials, is the prospect for varying the color of the device. Colors throughout the visible spectrum have been demonstrated in devices based on organic dye molecules, as well as polymer based devices.<sup>2-5</sup> There are different strategies for controlling the emission color of a material. In polymers the bandgap of the conjugated main chain can be varied by adding different side chains to the main chain. These substituents may affect the electronic structure, either by donating/ withdrawing electrons, or by introducing steric constraints upon the main chain and thus extending or shortening the effective conjugation length of the main chain. The regularity of the side chain incorporation strongly affects the band gap, as has been shown by several groups.<sup>6,7</sup>

We have used poly[3(4-octylphenyl)thiophene] (POPT) (Fig. 1) as the emitting material. This material, which is soluble in organic solvents but not fusible, has been reported before, but we obtain significantly enhanced properties in a modified synthetic route to the material. A thin film of POPT spin-coated from a chloroform solution has a metastable conformation. After heating the film, or treating it with chloroform vapour, a transformation of the polymer to a more ordered conformation occurs. The ordered polymer in the film shows a large red-shift of both light absorption and electroluminescence, compared to the metastable form of the polymer. The color of the film changes from red to purple and the electroluminescence shifts from orange-red to near infrared. This process is irreversible.

POPT was prepared by the route described by Andersson et al.<sup>9</sup> The main difference compared to the normal polymerization process with FeCl<sub>3</sub> is that the oxidant is added slowly to the monomer. In this way the oxidation potential is lower,

and a more selective polymerization reaction occurs. The polymer is carefully dedoped and purified by washing the polymer (dissolved in chloroform) with ammonia and water solutions of ethylenediaminetetraacetic acid (EDTA) several times. By  $^1$ H nuclear magnetic resonance the head-to-tail content was determined to be  $94\pm2\%$ . The molecular weight was determined to be  $M_n=23\,000$  (number average) and  $M_w=52\,000$  (weight average) by size exclusion chromatography (SEC) in tetrahydrofuran with polystyrene standards.

The light-emitting diodes were made by spin-coating the polymer onto indium tin oxide (ITO)/glass substrates from a chloroform solution (4 mg/ml). Film thicknesses of 400–1000 Å were investigated. A thin layer of calcium (200 Å) overcoated with a thick layer of aluminum (1000 Å) were used as the electron injecting contact. The metals were evaporated onto the film at a pressure less than  $4\times10^{-7}$  Torr. The aluminum was used to protect calcium from the ambient atmosphere. Device preparation and characterization were done in a laboratory environment.

Electrical and radiometric characterizations were made with a Keithley 617 electrometer and a Hamamatsu silicon photodiode (1010BR) together with a Keithley 485 picoampere meter. The quantum efficiency, emitted electrons per

$$C_8H_{17}$$
 $C_8H_{17}$ 
 $C_8H_{17}$ 
 $C_8H_{17}$ 

FIG. 1. Poly[3-(4-octylphenyl)thiophene] (POPT).

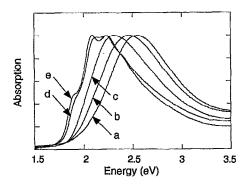


FIG. 2. Optical absorption of a POPT film. (a) Untreated film; (b) T=100 °C, 4 s; (c) T=100 °C, +8 s; (d) T=200 °C, +20 s; (e) T=200 °C, +30 s.

injected electrons, was estimated by using this photodiode. We have assumed Lambert emission of light, and the spectral response of the photo diode was taken into account. Luminescence spectra were taken with an Oriel Instaspec 1B diode array spectrometer. Absorption spectra were taken with a Perkin Elmer  $\lambda 9$  spectrophotometer. Film thicknesses were measured with a Sloan Dektak 3030.

After spin casting, the polymer is not in its equilibrium state. By simply exposing the film to chloroform vapor, or by a mild heat treatment, a transition occurs and the equilibrium state is obtained. The heat treatment is an easy way to control this conversion. By heating the spin coated polymer film on a hot plate, it was shown that it is possible to convert the polymer and shift the absorption maxima continuously. A spincast film has its absorption maxima at 2.55 eV (Fig. 2). After conversion it is found at 2.08 eV. It is possible to shift the absorption maxima continuously between these two states. Each intermediate state was stable over long times at room temperature. The structure in the absorption spectrum of the film closest to the equilibrium agrees with vibronic level separation of about 0.2 eV. 10,11 This might indicate that the polymer film is now in a more well ordered state. The absorption maximum of the fully converted film occurs at the second vibronic transition.

This shift of the absorption edge to lower energies is also reflected in EL (Fig. 3). To study this phenomenon an ITO/-POPT/Ca/Al device was heated on a hot plate. By using different temperatures and heating periods it is possible to control the color of the device from orange-red to the nearinfrared region. This corresponds to a shift of the EL maximum from 1.85 eV (670 nm) to 1.55 eV (800 nm). When the device was treated at higher temperatures and/or longer times at low temperatures, the spectra showed two vibronic peaks, similar to the absorption spectra. The vibronic peak at highest energy showed the highest intensity except for the two spectra where the device was heated at 200 °C. Here the vibronic peak at lowest energy showed the highest intensity. If the polymer film is treated with chloroform before evaporating the metal electrode, a similar spectrum with two distinct vibronic peaks is obtained. However, in this case the vibronic peak at lowest energy showed even higher relative intensity, compared to the vibronic peak at higher energy.

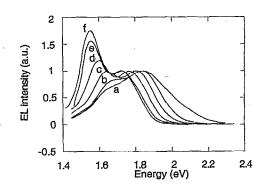


FIG. 3. Electroluminescence of an ITO/POPT/Ca/Al device for different heating temperatures. Curve (a) untreated device; (b)  $T=100\,^{\circ}\text{C}$ , 6 s; (c)  $100\,^{\circ}\text{C}$ , +6 s; (d)  $T=200\,^{\circ}\text{C}$ , +10 s; (e)  $T=200\,^{\circ}\text{C}$ , +20 s; (f) treated with chloroform before evaporating the contact.

The EL maximum of the chloroform treated device is also at 1.55 eV (800 nm).

The emission in the near infrared at 800 nm is, to the best of our knowledge, the lowest observed in polymer light emitting diodes. The next lowest are reported by the Cavendish group<sup>12</sup> at 710 nm from a derivative of poly(paraphenylenevinylene). The 800 nm emission is also the lowest energy EL reported so far in the thiophene system. The low bandgap of POPT is probably an effect of the regioregularity of the polymer chains. The low head-to-head content in POPT reduces the number of side group interactions and thus leads to an extended conjugation. This is further supported in a recent report on regular poly(3-butylthiophene), which shows an absorption spectrum similar to the spectrum of POPT. The effect of extended conjugation over the phenyl groups, relevant in POPT, is of minor importance according to calculations which show that they contribute at most 0.1 eV.<sup>13</sup> The very weak dependence of optical gap parameters on the coplanarity of phenyl side groups and thiophene rings on the main chain found in these calculations suggests that the shift of the bandgap is only due to an enhancement of the planarity of the main chain. Given that POPT is identical to the regioregular poly(3-butylthiophene), expected to be highly planar, and that the good agreement between theory, predicting an onset of absorption at 1.7 eV<sup>13</sup> in the fully planar polythiophene system, and experiment on POPT (and the P3BT), we propose that the blue form of POPT is the one of a planar main chain where side chains have been forced into a geometry consistent with this geometry. In the red form, planarity is prevented by steric interactions between side chains.

The mechanism for the heat or solvent induced transition from a high- to a low-bandgap material is not clear at present. The formation of the red phase during spinning is dependent on the rapid precipitation: this prompts us to conclude that this phase does not offer a global energy minimum. When enhancing the mobility of polymer chains, by exposure to solvent vapor or during heating, a new geometry may be obtained, giving a global energy minimum.

There are no differences in current-voltage characteristic between diodes made of films in different states. In Fig. 4 the

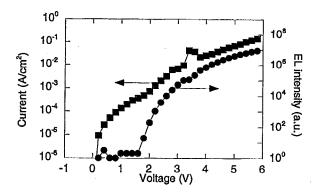


FIG. 4. I-V characteristics for an ITO/POPT(600 Å)/Ca/Al diode.

I-V characteristics for an ITO/POPT(600 Å)/Ca/Al diode are given. This is surprising, as the bandgap is shifting by almost 0.5 V. It might indicate that either the highest occupied molecular orbital (HOMO) or lowest unoccupied molecular orbital (LUMO) stay fixed during the conversion process, according to which state is giving the limiting step for injection of holes or electrons from the electrodes. It could also indicate that some other transport process is limiting, for instance transport across some thin insulating film at the metal contact. The emitted light is first detected at 1.8 V. At 2V the quantum efficiency is about 0.0002% and increases to 0.3% at 6 V. This compares well with the best results reported for other substituted polythiophenes.

We have been able to convert a substituted polythiophene, thermally or by solvent exposure, to decrease the bandgap, shifting electroluminescence into the near infrared. This widens the spectrum covered by light emitting polymer diodes considerably. The thermal control of bandgap narrowing allows a continuous variation of EL wavelengths.

We acknowledge helpful discussions with Mr. M. Boman and Dr. S. Stafström concerning optical spectra of conjugated polymers. This work was supported by the Swedish Engineering Research Council (TFR) and the Swedish National Board for Industrial and Technical Development (NUTEK).

- <sup>1</sup>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, 539
- <sup>2</sup>G. Grem, G. Leditzky, B. Ullrich, and G. Leising, Adv. Mater. 4, 36 (1992).
- <sup>3</sup>C. Zhang, S. Hoger, K. Pakbaz, F. Wudl, and A. J. Heeger, J. Electronic Mater. 22, 413 (1993).
- <sup>4</sup>Y. Ohmori, M. Uchida, K. Muro, and K. Yoshino, Jpn. J. Appl. Phys. 30, L1938 (1991).
- <sup>5</sup>D. Braun, G. Gustafsson, D. McBranch, and A. J. Heeger, J. Appl. Phys. 72, 564 (1992).
- <sup>6</sup>R. E. Gill, G. G. Malliaras, J. Wildeman, and G. Hadziioannou, 6, 132 (1994).
- <sup>7</sup>T. A. Chen and R. D. Rieke, Synth. Metals 60, 175 (1993).
- <sup>8</sup>Q. Pei, H. Järvinen, J. Laakso, and O. Inganäs, Macromolecules 25, 4297
- <sup>9</sup>M. R. Andersson, D. Selse, H. Järvinen, T. Hjertberg, O. Inganäs, O. Wennerström, and J. E. Österholm (unpublished).
- <sup>10</sup>H. Stubb, E. Punkka, and J. Paloheimo, Mater. Sci. Eng. Rep. 10, 85 (1993).
- 11 T. W. Hagler, K. Pakbaz, K. F. Voss, and A. J. Heeger, Phys. Rev. B 44, 8652 (1991).
- <sup>12</sup>N. G. Greenham, S. C. Moratti, D. D. C. Bradley, R. H. Friend, and A. B. Holmes, Nature 365, 628 (1993).
- <sup>13</sup>M. Boman and S. Stafström, Mol. Cryst. Liq. Cryst. (to be published).

1491