LIGHT EMITTING POLYMER MATERIALS: THE WORKING BASE FOR FLEXIBLE FULL COLOR DISPLAYS

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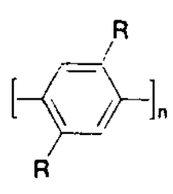
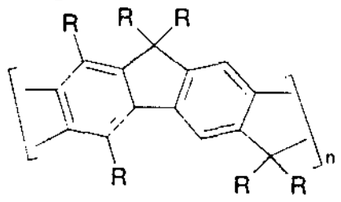
Abstract
Progress in light emitting materials is presented. New polymers based on the Spiro concept *show encouraging properties in electroluminescence performance and lifetime. The spiro-polymers can be tailor made to fit the RGB color requirements of a full color display. This class of materials showed recently very promising performance for white emission as well. They are readily soluble, show excellent thermal stability and can be processed by printing or through simple synthetic modification by photolithography technology.*

1. Introduction
Based on the outstanding performance and stability of spiro-materials in small molecule devices (OLEDs) [1], the spiro-concept was adopted for polymers as well. This paper summarizes the progress in synthesis and performance that has been made for poly-spiros.

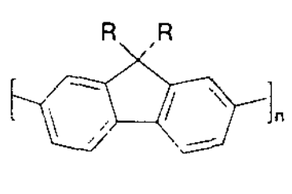
2. Concept
Classes of conjugated polymers that are able to emit blue light are known for some time. These include poly(*p*-phenylene)s (PPPs) [2], ladder-PPP [3] and polyfluorenes [4].



PPP



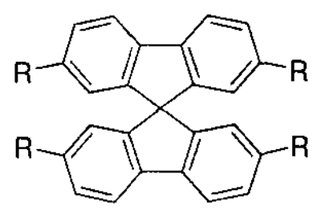
Ladder-PPP



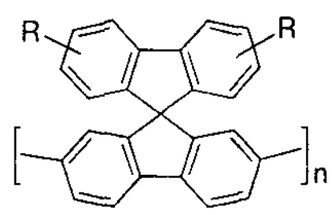
Poly-Fluorene

However, there are some fundamental problems that occur with extended aromatic structures of these types, the most important of which is that these long board-type structures tend to stack due to $\pi-\pi$ interactions between adjacent molecules. This leads to a number of practical disadvantages due to decreased solubility and sometimes even the formation of liquid crystal phases in solution [5], and unwanted bathochromic shifts of the electroluminescence caused by aggregate formation [6]. One approach to avoid these problems is the incorporation of sterically demanding groups into the polymer structure, which shield the main body of the polymer with their rigid geometry.

Small molecules based on the spiro-9,9-bifluorene unit show excellent performance in OLED devices [1], especially in terms of their temperature stability and their reluctance to crystallize. The latter is the direct consequence of the twisted molecular structure which makes $\pi-\pi$ stacking virtually impossible. The use of spiro- moieties as the base of a whole class of polymers results in materials that combine the potential for blue emission with the increased stability and stack-reducing properties of their small molecule relatives.



Spiros
(Small Molecule)



Poly-Spiros

The unique 3-dimensional arrangement (cf. Figure 1) of spiros reliably prevents polymer chains from aggregation. Furthermore, it leads to a very high temperature stability (T_g of poly-spiros are usually between 160°C and 230°C) and reliable film formation. The orthogonal biphenyl unit can be used for the introduction of additional functionality (dyes, charge transport units, solubilizing chains) and is offering a high degree of synthetic freedom.

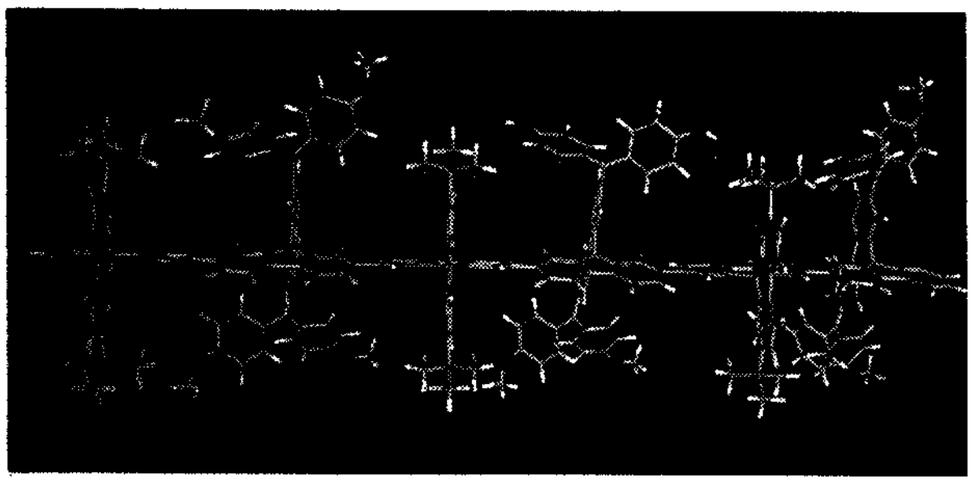


Figure 1 Molecular structure of a typical *poly*-spiro

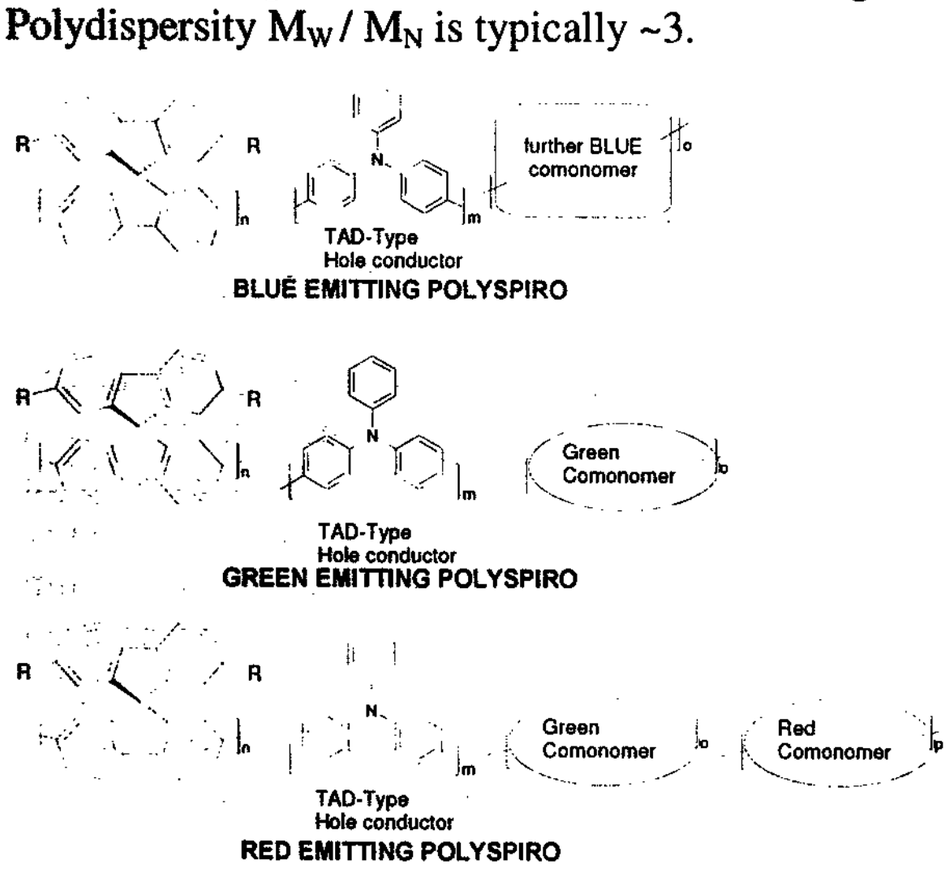
This paper reports on the synthesis and performance of *poly*-spiro molecules that feature red, green, blue and white electroluminescence.

3. Experimental

3.1 Synthesis

The synthesis of the monomers is described in detail elsewhere [7].

The synthesis of the (co)polymers was performed by optimized modifications of the Suzuki reaction [8] (starting from bis-bromides and bis-boronic esters) or the Yamamoto reaction (starting from bis-bromides) [9]. Molecular weights were usually between M_W = $5 \cdot 10^5$ to $1 \cdot 10^6$ g/mol and $M_N = 1.5 \cdot 10^5$ to $3 \cdot 10^5$ g/mol. Polydispersity M_W / M_N is typically ~3.



Scheme 1 Typical structures of RGB emitting POLY-SPIROS.

A large variety of polymers was synthesized using this general approach. Co-monomers were added for fine-tuning of the color and the injection/transporting properties.

3.2 Devices

Standard test LEDs were prepared according to the following procedure: ITO coated glass substrates were cleaned through repeated washing and plasma-treating steps. The buffer layer (20 nm Pedot or a Covion buffer layer) was spin-coated onto the substrate. The active polymer layer was coated from a 7-15 mg/ml solution in toluene. Cathode materials (usually 6 nm of Ba, followed by 100 nm of Ag) were then thermally evaporated in a vacuum chamber (pressure: 10^{-6} mbar). The layer thickness of the active layer was 80 nm, although in some cases higher efficiency and lower operating voltages were observed with thinner layers.

4. Results

All materials were evaluated in the Covion application lab in Frankfurt. The device structures for all PLEDs shown are exactly the same, and the polymer layer for each device is composed of a single copolymer, i.e. the polymer is not a blend.

4.1 Red Polymer

The RED POLY-SPIRO shows a deep red emission (x = 0.67, y = 0.33) with efficiencies of 2 cd/A and brightness levels of 100 cd/m^2 @ ~ 3.6 V, respectively 1000 cd/m^2 @ ~ 4.9 V are achieved. With a Covion buffer layer, the performance of this material were slightly improved in terms of efficiency (2.3 cd/A) as shown in figure 2 and lifetime improved with only 5% decrease of brightness after 400 h.

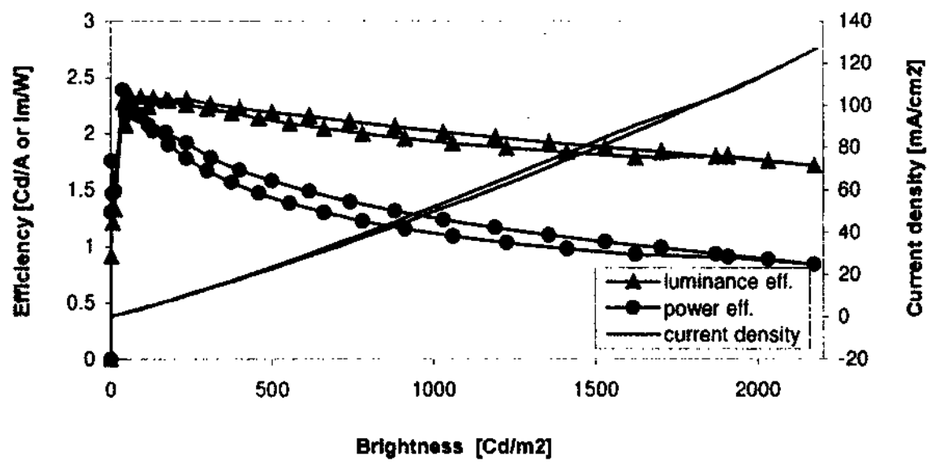


Figure 2 Performance data of a pure red emitting polymer (x = 0.67, y = 0.33)

4.2 Green Polymer

Reaching a pure green emission while maintaining high efficiency has been proven to be challenging. We developed green emitters particularly efficient for polyspiro polymers. These emitters lead to pure green emission (x = 0.33, y = 0.58), an efficiency of 14 cd/A and brightness levels of 100 cd/m^2 @ ~ 3.4 V. Using

an optimized ratio of co-monomers, adequate performance can be achieved (Figure 3).

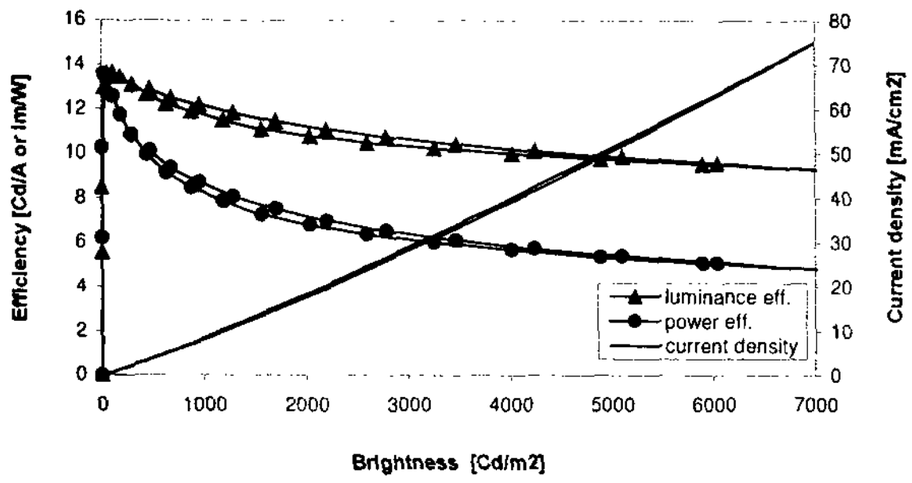


Figure 3 Performance data of a green emitting polymer (x = 0.33, y = 0.58)

4.3 Blue Polymer

For blue polymers, various derivatives have been prepared as well, allowing for different combinations of efficiency/color saturation. One example is shown in figure 4 with an efficiency of 4.4 cd/A and brightness levels of 100 cd/m^2 @ ~ 4.0 V.

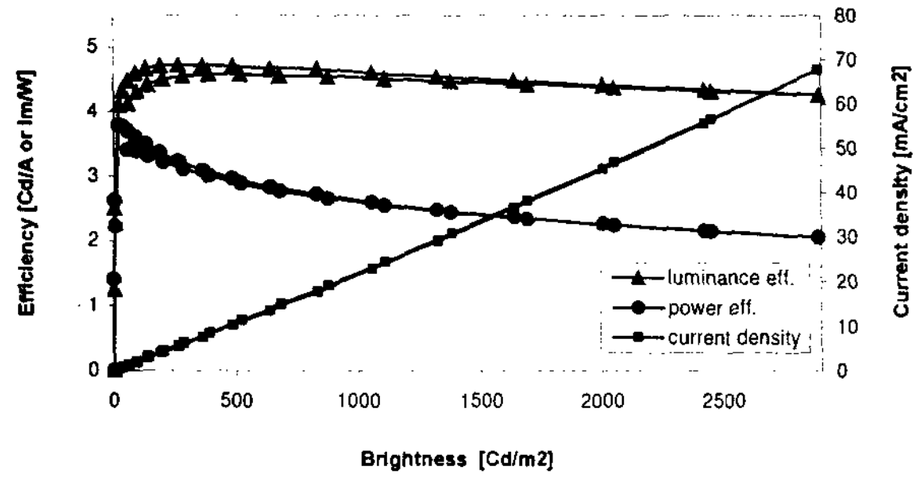


Figure 4 Performance data of a blue emitting polymer (x = 0.16, y = 0.19)

4.4 White polymer

Based on our experience with colored emitters in polyspiro, we succeeded in designing a white emitting co-polymer with an efficiency of 8 cd/A, brightness levels of 100 cd/m^2 @ ~ 4.2 V (figure 5) and presenting a very broad electroluminescence spectra (figure 6).

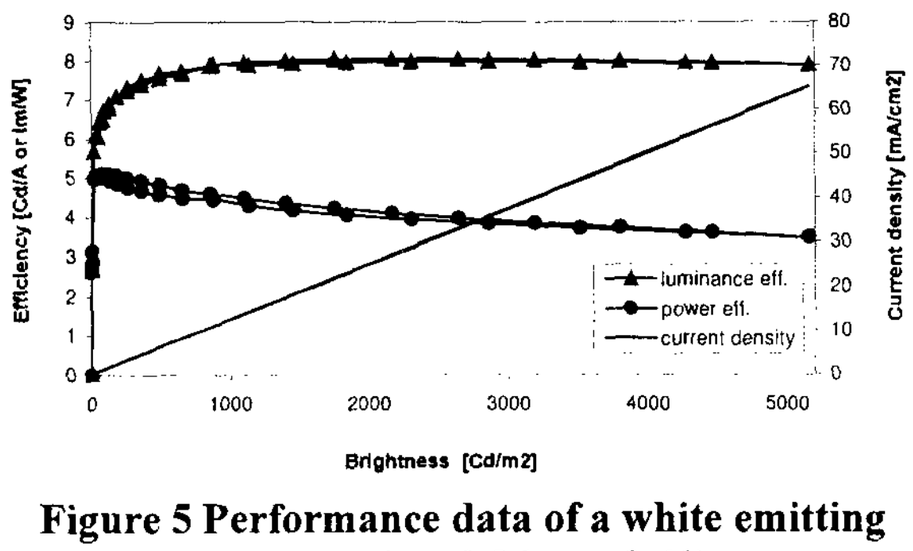


Figure 5 Performance data of a white emitting polymer (x = 0.36, y = 0.41)

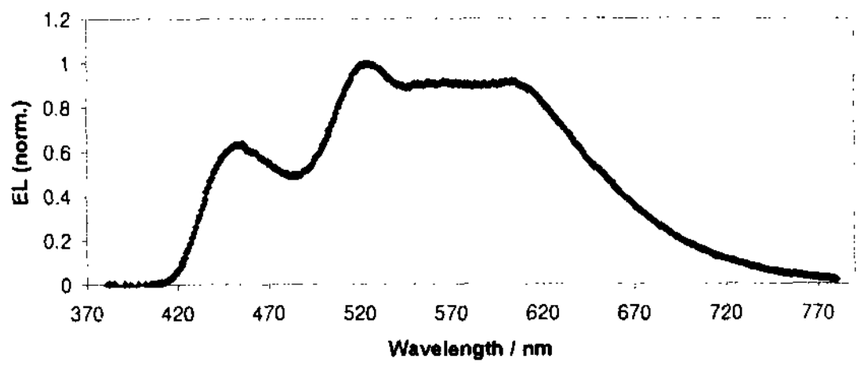
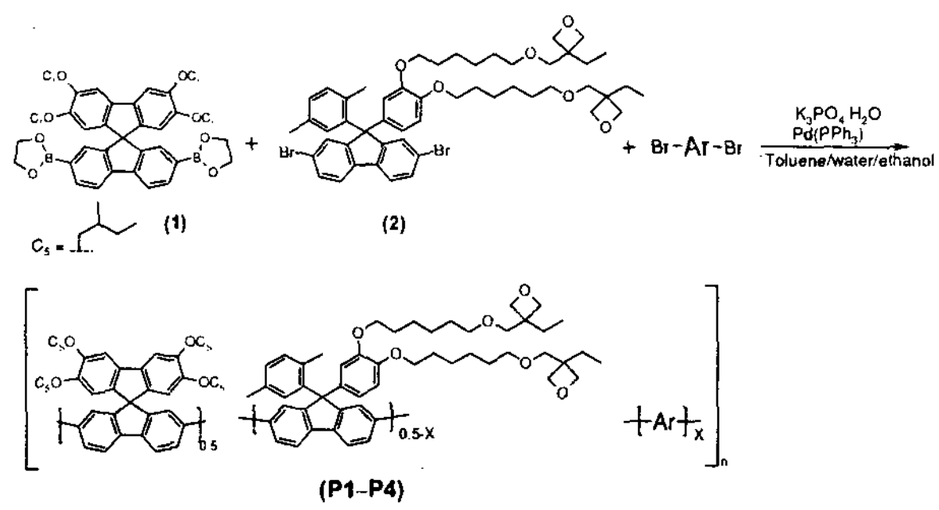


Figure 6 EL spectra of a white emitting polymer

5. Photolithography

We recently could demonstrate [10] the use of spiro-polymers, which can be patterned similarly to a standard photoresist. Soluble polymers with oxetane sidegroups were crosslinked photochemically to yield insoluble polymer networks in the desired areas. The resolution of the process is sufficient to fabricate common pixelated matrix displays. Consecutive deposition of the three colors yielded an RGB device with efficiencies and lifetimes comparable to state-of-the-art EL polymers with unchanged or even slightly reduced onset voltages.



Scheme 2 Synthetic procedure for crosslinkable EL polymers

Simple demonstration devices using this technique could already been shown. Resolutions in the µm range were possible using these X-linkable polymers.

The photoresist-type properties of the materials were investigated by irradiating through a shadow mask (grating; 250 μm period, 125 μm gap size). After curing, the films were developed by immersing them into THF, which re-dissolved the non-irradiated areas of the film. The line scan obtained with a profilometer (Figure 7) clearly demonstrated the formation of 125 μm wide ridges with sharp edges.

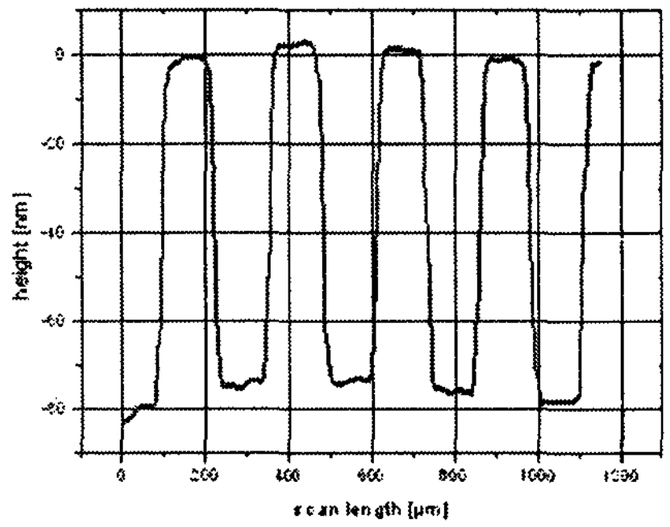


Figure 7 Profilometer line scan

The latter finding demonstrates that no significant diffusion of the photogenerated protons (generated by the photoacid) into the dark regions takes place. By applying the above-mentioned procedure three times, once for each polymer, we were able to fabricate pixelated devices with three individually addressable colors. The resolution of the patterning process was found (by holographic techniques) to be a few μm.

6. Summary

The new class of polymers presented will open up the display market for full color PLED displays. They span the required color gamut, show increasingly better lifetimes approaching commercially applicable stability, are soluble and thus can be deposited with the required spatial resolution through inkjetting or photolithography techniques, and can be provided in formulated solutions on a commercial scale. First passive matrix as well as active matrix full color demonstrator displays have already been manufactured by inkjet printing using these materials. With poly-spiros, full color inkjet printed displays seem feasible for the very near future.

7. Acknowledgements

The authors gratefully acknowledge the technical support of the whole *Covion* team. We particularly thank the PolyLed team of *Philips* and the team at *DuPont Displays* for the longstanding fruitful relationship.

8. References

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