Photochemically induced emission tuning of conductive polymers used in OLEDs

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Abstract. The present work focuses on the use of novel patterning technology schemes for the fabrication of OLED-based displays and in particular on the definition of two colour emitting pixels in one polymeric conducting layer. The approach adopted to this end is based on photochemically induced emission tuning. On the basis of this approach a novel photolithographic patterning technique was developed, aiming at the considerable simplification of the display fabrication process and on the performance improvement. We prepared electroluminescent devices that are emitting blue colour ($\lambda_{\text{max}}=413$ nm) with a turn-on voltage about 12-15V. In other devices we introduce a dispersed dye (1-[4-(dimethylamino)phenyl]-6-phenylhexatriene) and a series of photoacid generators (onium salts) in the polymeric layer and, by using an appropriate photochemical transformation through a photomask in a single layer, we were able to change the colour to desirable direction, since the parent compound and its photochemical product have distinguishable luminescence spectra (green and blue colour respectively). We were able to produce two of the three primary colours in a single layer of a conductive polymer by using a photochemical transformation based on photoacid induced emission change. A series of photoacid generators were evaluated.

1. Introduction

The possible use of OLEDs in display applications has been intensively investigated during the last years due to a number of attractive characteristics encountered in these devices, including possibilities for flexible display fabrication, low cost processing and emission tunability. In the context of this research effort a good number of conducting polymers and small organic molecule based materials with acceptable characteristics have been synthesized, following the pioneering work on small organic molecules by C. W. Tang et al. [1] and on PPV by the Cambridge group [2], and their successful use in device fabrication has been demonstrated in many cases [3-6].

Last years this continuing effort on development of OLED technology has started to lead to results capable for commercial exploitation and thus OLED-based products have entered the market in quite a few cases [7]. On the other hand the fabrication of organic OLED-based flexible displays has been also demonstrated but further technological developments are needed in this area in order to compete with existing inorganic material and liquid crystal based technologies. For instance, the generation of a full-colour image in a display requires the existence of nearby discrete areas, which are capable to emit one of the three primary colours i.e. red, green or blue. Several techniques have been appeared for producing the three colours needed in each pixel. In general, the manufacture of a full-colour display involves the formation of multi-layer structures that means, deposition and patterning of
different polymeric or small organic molecule based layers one over the other, where each one is capable of emitting one of the three-main colours. The deposition and patterning of each individual layer involves quite a few processing steps and in addition risks for performance degradation of the pre-existing layer during the deposition and patterning of the new layer. Several schemes have been proposed for the improvement of the whole process including selective diffusion of green and red dyes into adjacent regions, deposition of different materials by ink-jet printing and optical filtering of a single white-emitting OLED. Nevertheless, there is plenty of room for novel approaches that could lead to further performance advancement and cost reduction.

The present work refers to the development of novel patterning schemes for the fabrication of OLED-based displays, and in particular, targets at the definition of two-colour emitting pixels in one organic material layer. The approach adopted to this end is based on photochemically induced emission tuning, which is expected to result in considerable simplification of the OLED-based displays fabrication processes and on performance improvement.

2. Experimental
Materials and Instrumentation: 1-(4´-dimethyl-aminophenyl)-6-phenyl-1,3,5-hexatriene (DMA-DPH) was purchased from Lambda Probes and Diagnostics. The PMMA polymer used is Elvacite 2041 purchased from DuPont whereas the polyvinylcarbazole (PVK) was purchased from Aldrich. For absorption spectra the Perkin-Elmer Lambda-16 spectrophotometer was employed. Fluorescence and excitation spectra were recorded on a Perkin-Elmer LS-50B fluorometer. The fluorescence image pattern was photographed using a Nikon Microphot-FXA fluorescence microscope.

Polymeric Film Preparation and Processing: Solutions containing either the polymer Poly(methyl methacrylate) (PMMA) (2 % w/w on MethylIsoButylKetone-MIBK) or the PVK (40 mg/ml on 1,1,2,2 tetrachloroethane), an onium salt as photoacid generator (PAG) in various contents (2%, 4% and 8% of polymer mass) and the fluorescence probe DMA-DPH (1%, 2% and 4% of polymer mass) were prepared. Films were spin coated at 2000 r.p.m. and then baked on a hot plate at 110 °C for 1 min. Film thicknesses were measured with a Dektak profilometer (typical film thickness 100 nm). Photoacid generation was induced by exposing films with a 500 Watt Oriel Hg-Xe exposure tool through a 248 nm narrowband filter (6.5 nm half band width) for assessed times (see text). The incident power was 0.21±0.02 mJ/s.

3. Results and discussion
We were able to produce two of the three primary colours in a single polymer layer by a photochemically induced transformation. In particular a photoacid generator was used to induce emission change of the emitter, which in this case was dimethylaminodiphenylhexatriene DMA-DPH [8]. In figure 1 the principle of photochemically induced emission tuning is illustrated.

The UV/Vis absorption spectra of thin (100 nm) films prepared by spin-coating methyl iso butyl ketone (MIBK) solutions of PMMA containing DMA-DPH (2% w/w) and photoacid generators triflate 1 and 2 (4% w/w), on quartz substrate are shown in Figures 2 and 3 respectively. The characteristic absorption spectral changes obtained at different exposure doses are shown for the two different sensitizers, which have the same anion (triflate) but different cations. Upon subsequent irradiation with 248 nm light, photoacid generation is triggered and the absorption at the wavelength maximum (400 nm) of the neutral DMA-DPH form progressively decreases whereas a new structured band appears with a maximum at 361 nm. This is because protonation of the DMA-DPH molecule induces broadening of the absorption spectrum and shifts the wavelength maximum for about 20 nm hypsochromically.
The differences in absorption at the 250 nm area are due to the different cations. The efficiency of these two onium salts towards probe protonation is comparable. In figure 4 the corresponding changes in emission spectra of DMA-DPH emitter 2% in a PMMA matrix that also contains 4% onium salt (“triflate 2”) are shown.

Figure 1. Photochemically induced emission tuning of the DMA-DPH emitter.

Figure 2. Absorption spectral changes of DMA-PPH emitter in PMMA matrix through exposure at 248 nm in presence of “triflate 1” onium salt.

Figure 3. Absorption spectral changes of DMA-PPH emitter in PMMA matrix through exposure at 248 nm in presence of “triflate 2” onium salt.

In figure 5 a successful experiment of emission change of poly vinyl carbazole (PVK) is presented by using the emitter DMA-DPH and the photoacid generator “triflate 2”. Thus, in this case it is shown that the photogenerated acid indeed protonates quantitatively the probe and not the PVK polymer nitrogen groups.

Films of similar composition as above (containing DMA-PPH, and “triflate 2” in PVK) where also tested as active materials of light emitting diodes. Characteristic IVs obtained with pure PVK and PVK congaing the probe and the sensitizer are presented in Figure 6. From this figure it is evidence that the addition of the sensitizer and the probe –resulting to the formation of the “green” polymer– does not affect the electrical behaviour of the polymer matrix (blue PVK). On the contrary a slight improvement of contrast curve is seen.
4. Conclusions

Two-color single layer organic light emitting diodes (OLEDs) were fabricated with the insertion of a suitable emitter in a blue polymer (PVK), which allows the tuning of electroluminescence spectrum by energy transfer to this emitter. The selected emitter was dispersed in the electroluminescent films and their emission was tuned through photochemically induced transformations and thus we were able through a photomask to define areas in a single layer that emit blue or green light. Component selection and stability (life time) of photochemically induced emission properties studies were carried out.

5. References

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