

Tuning the Electroluminescence Color in Polymer Light-Emitting Devices Using the Thiol-Ene Photoreaction**

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Laterally patterning the emission color of polymer light-emitting devices is one of the current technological challenges for their commercialization. Photopatterning is one of the most convenient approaches for the production of closely spaced, differently colored pixels, other than direct-writing approaches such as ink-jet printing. The photo-induced addition of thiols to C=C bonds (the thiol-ene) reaction is here utilized to achieve photobleaching of poly(phenylenevinylene)-type polymers. By exploiting the chemical selectivity of the UV-induced thiol-ene reaction, the emission color in a guest–host system is tuned from that of the guest to that of the host. It is demonstrated that the presented method can be applied for numerous energy-transfer systems.

1. Introduction

Since their invention more than a decade ago,^[1] polymer light-emitting devices (PLEDs) have received ample attention. Emission colors covering the whole visible spectral range have been realized. For full-color display applications, red, green, and blue pixels have to be fabricated next to each other with considerable spatial resolution. Realization schemes for this challenge include external conversion layers^[2] and filters,^[3] solvent-enhanced dye diffusion,^[4] or printing techniques such as screen-^[5] and ink-jet printing.^[6]

Lately, alternative patterning approaches^[7–9] for conjugated polymers have been presented. In particular, photopatterning techniques that influence the active layer itself, an alternative to using a photoresist to define a pattern, have been demonstrated. The advantage of these methods over direct writing strategies is the possibility of employing conventional coating procedures (such as spin-casting) to achieve good uniformity of

the active layer. Full-color photopatterned light-emitting devices have been presented by Shirai and Kido,^[10] who used laser irradiation to (oxidatively) bleach dye molecules in a poly(*N*-vinylcarbazole) matrix. In a different approach, Müller et al.^[11] were able to demonstrate red–green–blue (RGB) devices by sequential spin-casting of red-, green-, and blue-emitting polymers, immobilizing them on the substrate by photocrosslinking and removing the non-crosslinked remnants with a solvent before spin-casting the next polymer.

In our approach, only a single polymer layer, containing a blend of fully conjugated polymers, has to be spin-cast. This allows one to conserve material that would be otherwise lost in successive spin-coating procedures. The lower-bandgap components of the layer are then photochemically modified, to bleach their emission. The most straightforward way to achieve this would be to oxidatively bleach the materials. This is, however, detrimental to the performance of PLEDs, as the carbonyl-type groups created act to quench^[12] or spectrally alter the emission.^[13] Thus, while oxidative bleaching of conjugated polymers could, in principle, be used for monochromic displays,^[8] multi-colored applications call for a different patterning reagent. It is essential that this reagent will photochemically and selectively bleach one or more components of the blend, while not electronically coupling^[14] to the conjugated backbone of the polymer, as is the case for carbonylic sites occurring in oxidative patterning.

In recent contributions, we have demonstrated that gaseous hydrazine is suitable as the reagent, to obtain multi-colored^[15] and red-, green-, and blue-emitting PLEDs.^[16] We have shown, that a photoreaction with hydrazine can be used to selectively saturate (hydrogenate) the vinylene groups in a poly(*p*-phenylenevinylene) (PPV) chain, leaving the aromatic units intact up to long UV exposure times.^[17] Exploiting this chemical selectivity, we have shown that the total electroluminescence (EL) color of thin films, consisting of a poly-aromatic (blue-emitting) host and a (lower-bandgap) guest polymer containing vinylene units, can be changed from the emission color of the guest to

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that of the host by exposing the film to UV irradiation in the presence of hydrazine.

However, photopatterning processes employing gaseous hydrazine pose three major problems. First, hydrazine is a highly toxic compound, which would be problematic in an industrial environment. Second, for long exposure times, the aromatic units of the host could also be hydrogenated. Third, hydrazine is scarcely soluble in apolar polymers which limits the process to very thin films. To overcome these difficulties, we have explored alternative photochemical reactions that might be employed for UV-induced patterning processes suitable for PLED applications. The present contribution focuses on the photo-induced reactions of alkane thiols with PPV-type conjugated polymers. It will be demonstrated that these compounds are viable alternatives to hydrazine as the reactive agent for the patterning of multi-color PLEDs.

2. Results and Discussion

2.1. Photo-induced Reactions of Thiols with PPV-Type Polymers

The addition reaction between thiols and olefins to give thioethers ("thiol-ene" reaction) has been known for some time^[18] and both ionic and free-radical mechanisms are recognized.^[19] However, in most cases a free-radical reaction is carried out and both thermal and photochemical initiation have been described. The UV absorption of aliphatic thiols extends to 275 nm; the bond energy of the S–H group in aliphatic thiols amounts to ca. 230 kJ mol⁻¹. Using a free-radical initiator, the reaction rate of the thiol-ene reaction can be increased significantly and a chain reaction is observed.^[19,20]

While most of the literature on thiol-ene reactions refers to the synthesis of low-molecular-weight thioethers, some applications for the modification of unsaturated polymers such as poly(1,2-butadiene) have been reported.^[21] To our knowledge, the thiol-ene reaction has not been utilized to modify conjugated polymers of the PPV type as yet.

To start with, the reaction of dodecanethiol and poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV) was investigated. Mixtures of MEH-PPV and dodecanethiol were spin-cast as described in the Experimental section and subjected to UV irradiation. In this case, a free-radical photoinitiator (2-hydroxy-2-methylpropiophenone) was added at a concentration of 1 wt.-%. Figure 1 shows the UV-vis absorption spectrum of MEH-PPV containing 4 mol of dodecanethiol per equivalent of vinylenes before and after UV irradiation under inert-gas conditions. The absorption decreases as a result of the UV illumination and after 40 s the bleaching process is complete. In a control experiment, MEH-PPV was illuminated in the absence of dodecanethiol. As expected, this did not cause significant changes in the UV-vis spectrum of MEH-PPV.

In a similar experiment, the use of a gaseous thiol (2-propanethiol) was investigated. In these experiments no photoinitiator was employed. Again efficient bleaching of the UV-vis ab-

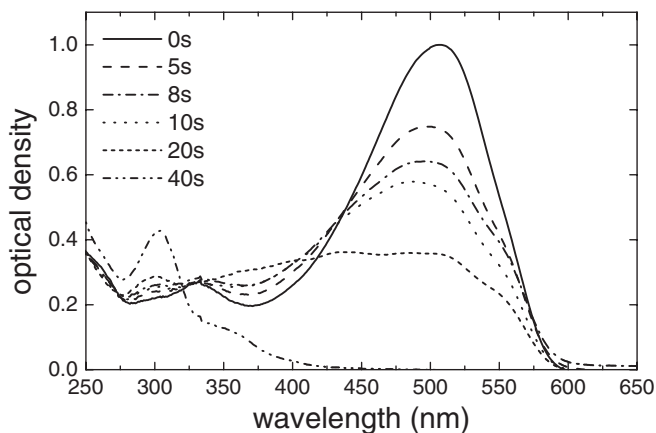


Figure 1. Absorption spectra of a MEH-PPV film loaded with dodecanethiol as a function of the UV exposure time.

sorption was observed. Figure 2 shows Fourier-transform infrared (FTIR) spectra of a film of MEH-PPV (100 nm) prior to and after UV illumination under nitrogen-containing vapor of 2-propanethiol. The FTIR signals at 3060, 1352, 1254 and 969 cm⁻¹ disappear, which indicates a saturation of the C=C double bonds in the polymer main chain. At the same time, the FTIR signals in the range 2800–3000 cm⁻¹ (C–H valence vibration of aliphatic units) increase in intensity.

From these data it becomes apparent that a saturation of the vinylenes proceeds during the reaction of MEH-PPV with thiols. Basically this could be the result of a photo-induced thiol-ene reaction; however, a photo-induced hydrogenation and a cycloaddition of C=C double bonds would also give similar results in the UV-vis and FTIR spectra. For instance, a hydrogenation has been observed for the photo-induced reaction of benzeneselenol with stilbene which almost exclusively yields diphenylethane.^[22] To clarify this, X-ray photoelectron spectroscopy (XPS) was employed to characterize the surface of an MEH-PPV film. Figure 3 displays XP spectra of MEH-PPV films after different UV irradiation times (up to 120 s) in the

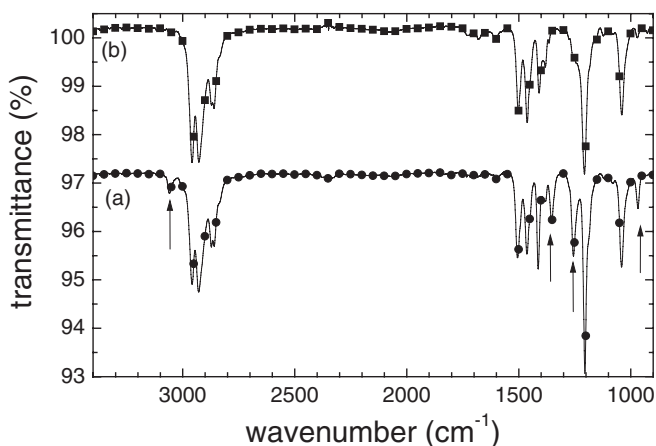


Figure 2. IR spectra of a pristine film of MEH-PPV (a), and a film exposed to UV irradiation in the presence of gaseous 2-propanethiol for 120 s (b). The spectra have been offset for clarity. The arrows indicate spectral changes.

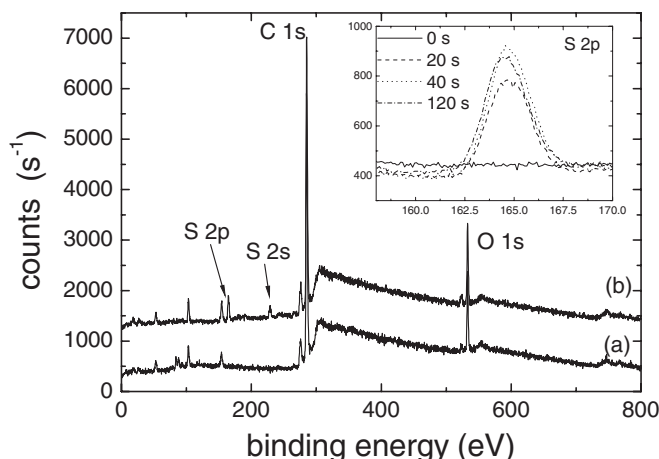


Figure 3. XPS spectra of a pristine film of MEH-PPV (a), and a film exposed to UV irradiation in the presence of gaseous 2-propanethiol for 40 s (b). The spectra have been offset for clarity. The inset shows the evolution of the S 2p peak as a function of UV exposure time.

presence of 2-propanethiol. The S 2p signal (164.5 eV) and the S 2s signal at 229 eV are absent before irradiation but are easily discernible after the photoreaction. This result shows that sulfur-containing groups are present at the surface of MEH-PPV as a result of UV irradiation in the presence of 2-propanethiol. A quantitative interpretation of the XP data showed that the content of sulfur amounted to 4.7 at.-% (hydrogen is omitted in this calculation). This equals one sulfur atom per repeating unit in the polymer chain. The XPS data thus indicate that — at least at the surface of MEH-PPV — a thiol-ene reaction proceeds as outlined in Figure 4.

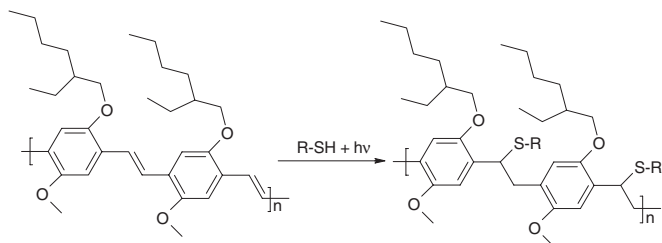


Figure 4. Proposed photoreaction of MEH-PPV with an alkanethiol.

2.2. Selective Bleaching of PPV in a Polyfluorene Matrix

To demonstrate the feasibility of selective photobleaching, we prepared thin films of a blend of poly(9,9'-dioctylfluorene) (PF8) with MEH-PPV (weight ratio 9:1) loaded with dodecanethiol. These films were exposed to UV radiation under inert-gas conditions. The absorption and photoluminescence (PL) spectra of the pristine films and the exposed films are shown in Figure 5. At zero exposure time, the absorption spectrum is a superposition of the absorption of MEH-PPV (from 2.1 to 2.7 eV) and PF8 (higher energies). We note, that the PF8 absorption band shows two peaks: a strong maximum centered at 3.1 eV and a weaker one at 2.85 eV. The main peak

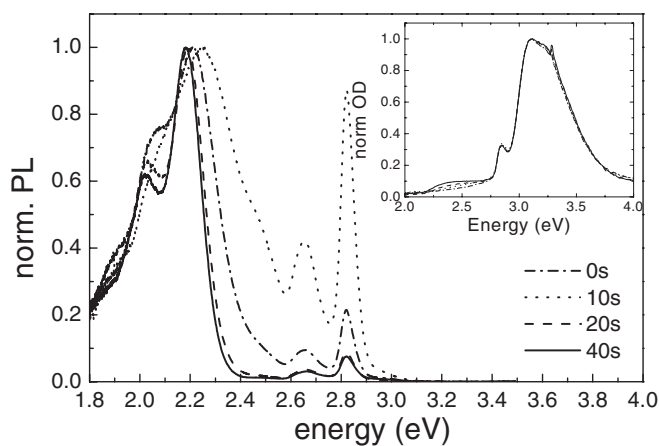


Figure 5. PL spectra of a thin solid film of aPF8:MEH-PPV (9:1) blend containing dodecanethiol after 0, 10, 20, and 40 s of polychromatic UV irradiation (residual dodecanethiol had been extracted from the film under vacuum before the spectra were recorded). The spectra have been recorded for excitation within the π - π^* band of PF8. The inset shows the corresponding optical densities of the film for different UV exposure times.

corresponds to the π - π^* transition commonly observed for films of poly(fluorene)-type materials. The smaller peak has been assigned to the so-called β -phase found in PF8 upon, e.g., thermal cycling, annealing, or solvent-vapor exposure.^[23,24] This β -phase is characterized by a planarization of the poly(fluorene) backbone as a result of side-chain crystallization.^[23] It constitutes a lower-bandgap phase within the poly(fluorene); correspondingly, the PF8 emission band is dominated by β -phase emission. In the pristine blend, containing 10 wt.-% of MEH-PPV, most of the emission observed from the polymer film stems from MEH-PPV when exciting within the π - π^* -band of PF8. This demonstrates efficient energy transfer between the two materials. Aggregation of MEH-PPV chains seems to be minor as the emission spectrum of MEH-PPV corresponds closely to the solution spectrum providing evidence that the MEH-PPV chains are dissolved in the PF8 matrix.

As a result of the UV-induced thiol-ene reaction between dodecanethiol and MEH-PPV, we observe a decrease of the MEH-PPV absorption band with increasing exposure time. A concomitant decrease in relative PL intensity from MEH-PPV is observed. The decrease in PL from MEH-PPV is accompanied by a blue-shift of its emission band, indicative of a reduction of conjugation length. Thus, we observe that the emission color of a blend system of PF8 and MEH-PPV can indeed be tuned by a variation of the UV exposure time using a liquid-thiol reagent.

Investigating the optical spectra of films which were spin-cast from the PF8:MEH-PPV blend without the addition of a liquid thiol, we did not observe β -phase formation in PF8. In a control experiment, in which the neat polymer film (no thiol added) was irradiated under nitrogen, no bleaching of the MEH-PPV component was observed for the exposure times reported below. To test the selectivity of the thiol-ene reaction using a gaseous reagent, the PF8:MEH-PPV films were exposed to UV irradiation in the presence of 2-propanethiol. The

results are shown in Figure 6. The emission spectrum recorded for the film exposed for 10 s corresponds to that of β -phase PF8, and no emission from MEH-PPV is visible. We thus observe that the bleaching effect achieved by 40 s for patterning using a liquid reagent is surpassed by the patterning with the gaseous reagent for exposure times of 10 s under otherwise identical conditions. This is most likely a result of the greater diffusional mobility of 2-propanethiol in the polymer layer.

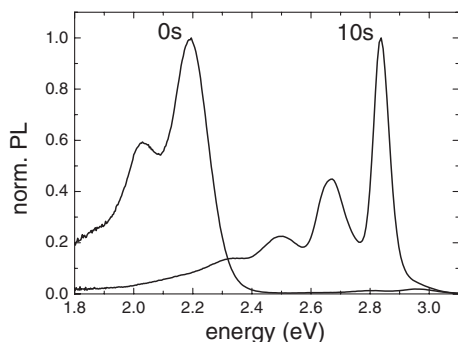


Figure 6. PL spectra of a thin solid film of a PF8:MEH-PPV (9:1) blend prior to and after 10 s of polychromatic UV irradiation in the presence of gaseous 2-propanethiol. The spectra have been recorded for excitation within the π - π^* band of PF8.

As mentioned above, the poly(fluorene) emission after photopatterning in the presence of gaseous 2-propanethiol is purely β -phase emission. We have investigated the influence of the patterning process on the β -phase formation. To separate the effects of UV irradiation and the interaction of the polymer with 2-propanethiol vapor, we have measured the emission and excitation spectra of a) pristine PF8 films, b) films of PF8 that were exposed to UV radiation under N_2 , c) films of PF8 exposed to 2-propanethiol vapor under N_2 , and d) films of PF8 irradiated with UV light in the presence of 2-propanethiol under N_2 . The results before and after the treatments are shown in Figure 7. We observe that only the combination of a gaseous thiol and UV exposure leads to an efficient β -phase formation. This can be rationalized by assuming that 2-propanethiol acts

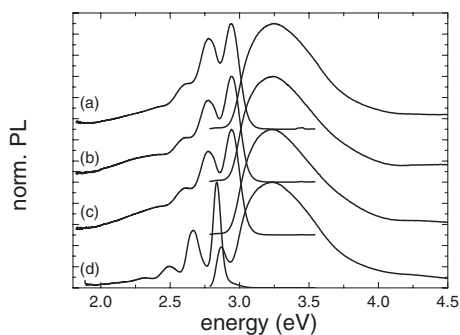


Figure 7. PL and PL excitation spectra of thin solid films of PF8. The spectra have been recorded for the pristine film (a), a film exposed to 2-propanethiol in the dark (b), a film irradiated with UV under N_2 flow (c), and a film exposed to UV irradiation in the presence of gaseous 2-propanethiol (d).

as a (weak) solvent for PF8. The fact that UV light is needed for the phase transition can be explained by a slight heating during UV irradiation, which can accelerate the recrystallization process. Our patterning approach thus results in a modification of the polymer morphology similar to that observed for solvent-vapor treatment.^[23] For actual applications of the presented photopatterning method it will be advantageous to use poly(fluorene)s with branched side chains, which do not show a β -phase,^[25] to achieve a saturated blue emission color.

2.3. Device Applications

Dual-color PLEDs were manufactured using both patterning approaches (liquid and gaseous thiols). Bleaching the lower-bandgap component using 2-propanethiol in the gas phase, however, resulted in more efficient and more stable devices. This is most probably explained by inhomogeneities in the polymer film, which are incurred in the removal process of the excess dodecanethiol under vacuum. Therefore, only devices fabricated using 2-propanethiol as the reactive compound will be discussed below.

The simplest multicolor device can be realized from a blend of two materials. We have used a blend of PF8 and MEH-PPV (99:1 weight ratio) to produce a conjugated polymer film on a poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)-covered indium tin oxide (ITO) substrate. The sample was exposed to gaseous 2-propanethiol as outlined in the Experimental section. During UV irradiation, half of the substrate was shadow masked. Figure 8 shows the current-voltage and the luminance-voltage characteristics of two PLEDs, one within the illuminated substrate area, the other in the shadow-masked area. The current-voltage characteristics are identical within the commonly observed variance between PLEDs fabricated under nominally equal conditions. The onset voltage for EL (ca. 4 V) increased by approximately 1 V com-

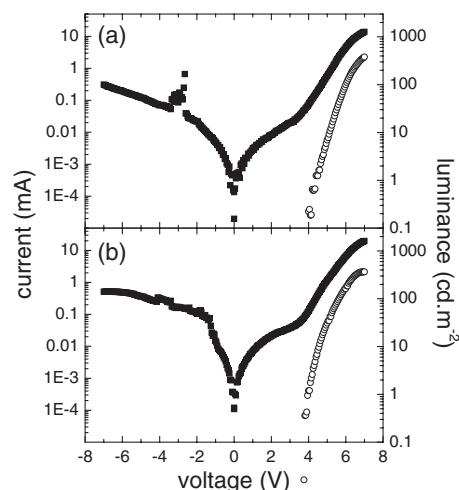


Figure 8. Device characteristics of a PLED fabricated from a blend of PF8 and MEH-PPV (99:1 by weight). a) The characteristics of a non-bleached device. b) The characteristics of a device that had been subjected to 10 s of UV irradiation in the presence of 2-propanethiol.

pared to control samples (not shown) that were not exposed to the thiol-containing atmosphere. Preliminary experiments indicate that this results from dedoping of the PEDOT:PSS layer by the thiol, which occurs independently of the UV irradiation. Experiments are currently underway to improve our understanding of this process. The current–voltage characteristics (Fig. 8), however, demonstrate that the devices are hardly affected by the bleaching process (i.e., UV exposure), as the photo-induced thiol-ene reaction affects only the minority component of the blend (MEH-PPV), and thus has little to no effect on charge injection into and charge transport in PF8. No apparent detrimental effects on the device lifetime were observed. More extensive testing is currently being performed.

The EL spectra of the two PLEDs are shown in Figure 9. For the un-illuminated PLED, the spectrum is dominated by emission from MEH-PPV peaking around 2.1 eV, with Commission Internationale d'Eclairage (CIE) color coordinates of (0.4,0.4). When comparing the relative intensities between photo- (Fig. 6) and electroluminescence (Fig. 9), one notices that for EL the contribution from MEH-PPV is of the same order of magnitude as for PL, despite the considerably reduced concentration of MEH-PPV in PF8 for the EL experiments (weight ratios of 9:1 and 99:1, respectively). This is attributed to charge-carrier trapping and thereby enhanced recombination on the low-bandgap component of the blend.^[26] After photopatterning, the EL spectrum corresponds to that of PF8 with CIE coordinates of (0.16,0.12). This demonstrates that the photo-induced thiol-ene reaction can be used to fabricate dual-colored PLEDs.

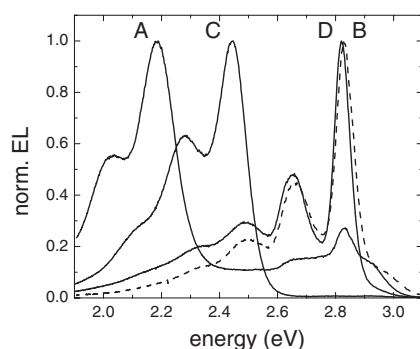


Figure 9. EL spectra of two-component PLEDs. Spectra A and B: emission spectra of PF8:MEH-PPV (99:1) PLEDs, one of which was exposed to UV-illumination in the presence of 2-propanthiol for 10 s. The spectra correspond to the device characteristics in Figure 8. Spectra C and D: emission spectra of PF8:GE (95:5) PLEDs. The PLED for spectrum D has been exposed to UV irradiation (20 s) in the presence of 2-propanethiol.

The patterning process is not limited to the combination of the materials discussed above, as long as the premise of a poly-aromatic host with a material containing vinylene units in the conjugated backbone as a guest material is followed. As another example, we demonstrate that the emission color of a blend of an alternating copolymer of poly(fluorene) and MEH-PPV (termed GE) and PF8 (5:95) is tunable from green to blue by 20 s of photopatterning (EL spectra, see Fig. 9). Maximum

luminance values of 580 cd m^{-2} at 0.2 A cm^{-2} for the green device and 310 cd m^{-2} at 0.36 A cm^{-2} for the blue device could be achieved.

As the emission color of a blend of two materials is only tunable along the line connecting the color coordinates of the components,^[27,28] a third component has to be added to the blend to increase color range and render full-color emission possible. Previously^[16] we have described that for the hydrazine photobleaching process, the addition of a third component (a cyano-substituted fluorene/phenylene vinylene copolymer) could indeed be used to achieve red, green, and blue emission colors from a single polymer blend. For the thiol-ene photoreaction described in the present contribution, we found that the red-emitting polymer used in previous work^[16] shows a lower susceptibility to the thiol-ene photoreaction than the green emitter. Thus, as the green and the red emitter are simultaneously affected by the photopatterning; the previously red emission of the blend was directly converted to blue emission for patterning using the thiol-ene photoreaction. Therefore, the combination of materials used in the previous work^[16] cannot be used for thiol-ene photopatterning. Still, the thiol-ene photopatterning is, in principle, applicable to more complex energy-transfer systems. To extend the color range of the demonstrated devices, an alternate third component (MEH-PPV) was used. A polymer blend of PF8:GE:MEH-PPV 93:5:2 by weight was used to fabricate orange-emitting devices. In Figure 10, we show the EL spectra for an unpatterned device, as well as two devices exposed to UV irradiation under 2-propanethiol for 5 s and 20 s, respectively.

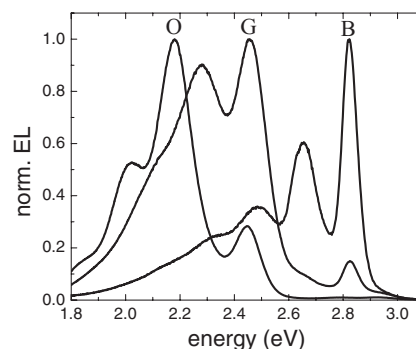


Figure 10. PLEDs with various emission colors realized by thiol-ene photopatterning employing gaseous 2-propanethiol. The lower graph shows the corresponding EL spectra. The UV exposure times were 0 s, 5 s, and 20 s, respectively.

We observe that for the unexposed device the emission color is dominated by emission from MEH-PPV. By the photopatterning process, we recover the emission of GE (exposure time 5 s), as most MEH-PPV chains have been bleached and enough (conjugated) GE segments remain to dominate the emission color. For longer exposure times, we are able to recover the blue emission color of PF8. Expressed in CIE coordinates, these spectra correspond to (0.45,0.51) for the non-bleached blend system, (0.31,0.53) for 5 s exposure, and (0.19,0.20) for 20 s exposure. The electrical characteristics of

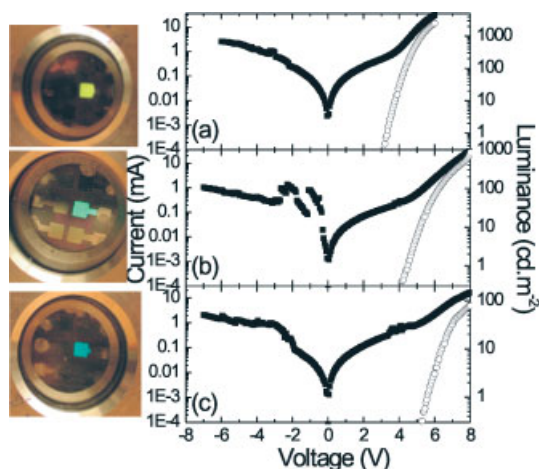


Figure 11. Current–luminance–voltage characteristics of PLEDs fabricated from a three-component system PF8:GE:MEH-PPV (93:5:2). a) Pristine blend (not-exposed to the thiol containing atmosphere). b) The PLED after 5 s and 20 s of photobleaching in the presence of gaseous 2-propanethiol.

the corresponding devices are shown in Figure 11. We observe an increase in the onset voltage from the device, that has been exposed to neither the thiol atmosphere nor to UV irradiation (Fig. 11a), to the one exposed to 5 s of UV irradiation in the presence of 2-propanethiol (Fig. 11b). As indicated above, this is ascribed to a partial dedoping of the PEDOT:PSS layer by the alkanethiol. A decrease in luminous efficiency between the pristine and the 5 s irradiated device is also attributed to the impact the dedoping of the PEDOT:PSS layer has on the device performance. The device efficiency further decreases for the device that has been patterned for 20 s (Fig. 11c). The further decrease is partially attributable to the fact that the eye's sensitivity is considerably lower in the blue than in the green spectral region. The increase in onset voltage might be due to a change of the polymer surface during photopatterning (this is currently being investigated). It should be noted that by affecting 7 % of the active layer, the current densities for the blue-emitting device are markedly lower than for the green-emitting one.

3. Conclusion

In conclusion, we have found that alkane thiols can be added to the vinylene unit of PPV-type polymers under UV irradiation (thiol-ene reaction). The formation of this species interrupts the conjugation of the polymer at that position and effectively bleaches the π - π^* transition of the PPV-type polymer. The reaction is highly selective towards the vinylene units. Therefore, in blend systems consisting of a poly-aromatic host and a PPV-type guest material the emission color was tuned from that of the guest to that of the host.

Multi-colored PLEDs, fabricated using the thiol-ene photo-reaction to tune the emission properties, have been demonstrated. The patterning process can be implemented at low cost, and requires moderate light intensities for high patterning

speeds. It was also shown that it is possible to avoid gaseous reagents by adding liquid thiols, such as dodecanethiol, to the polymer blend. Compared to the previously reported process using hydrazine, thiols are advantageous due to their better compatibility (i.e., solubility) in apolar polymers and their lower toxicity. However, the unpleasant smell of thiols requires specific measures during handling.

Achieving color tunability beyond dual-color devices calls for an optimization of guest systems (using lower concentrations of the guests). It will also be necessary to aim for greater chemical selectivity of the photoreaction. We are confident that the photopatterning method presented in this contribution, once the remaining issues have been overcome, will be attractive for the production of low-cost PLED applications.

4. Experimental

4.1. Materials

The polymers that were used in this study were poly(9,9'-dioctyl fluorene) (PF8), poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV), and an alternating copolymer of poly(fluorene) and MEH-PPV, emitting in the green spectral region (compare [16]), in the following termed GE. They serve to cover a range of colors ranging from blue (PF8) to orange (MEH-PPV). All polymers were purchased from American Dye Source Inc. [29]. 2-Propanethiol (>99 %) and 1-dodecanethiol (>97 %) were purchased from Fluka.

4.2. UV-Induced Bleaching

The polymer samples were placed in a reaction chamber equipped with a quartz window. This reaction chamber was then flushed with nitrogen to exclude any traces of oxygen. For photoreactions using 2-propanethiol as reagent, a stream of dry nitrogen was passed through liquid 2-propanethiol (boiling point 57–60 °C). The nitrogen stream (loaded with 2-propanethiol vapor) was then passed through the reaction chamber containing the polymer sample. For UV irradiation, the unfiltered light of a 1300 W high-pressure Hg lamp was used. The power density at the sample surface was measured with a spectroradiometer (Sola-Scope 2000 from Solatel). At 254 nm the spectral intensity amounted to 2 mW cm⁻². For the polymer samples containing dodecanethiol as a reactive component, UV irradiation was carried out under a nitrogen atmosphere.

4.3. Sample Preparation

For the photoluminescence (PL) experiments, chloroform solutions containing 2 g L⁻¹ of the polymer blend in chloroform were prepared. When using dodecanethiol as the reactive agent, this compound was added to the polymer solution at a concentration of 4 mol of dodecanethiol per mole of C=C double bonds (of PPV) [30]. Thin polymer films were prepared by spin-casting the solutions onto quartz or CaF₂ substrates. After irradiation, residual dodecanethiol was removed by heating the samples to 75 °C in vacuo (<10⁻⁴ mbar).

4.4. Sample Characterization

Absorption spectra were measured using a Perkin-Elmer λ 9 transmission spectrometer. PL spectra were recorded using a Shimadzu

RF5301PC spectrophotometer calibrated using an Ocean Optics LS-1-CAL light source. Infrared absorption spectra were recorded with a Perkin–Elmer SpectrumOne FTIR spectrometer. XP spectra were recorded for films spin-cast onto gold-coated substrates using a Kratos XSAM800 spectrometer using Mg K α radiation.

4.5. Device Fabrication

PLEDs were fabricated on indium tin oxide (ITO)-covered glass substrates, onto which thin films of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, Baytron P from Bayer Inc.) were spin-cast and dried at 120 °C for 2 h under inert-gas conditions. The conjugated polymers were dissolved in chloroform (concentration of 5 g L⁻¹) and stirred overnight. The polymer blend was spin-cast onto the dry PEDOT:PSS layer. The thiol-ene photoreaction was carried out as described above. The samples were thereafter dried at 70 °C under vacuum for a minimum of four hours. Calcium electrodes covered by an aluminum capping layer were deposited in a Baltzers MED010 vacuum coating apparatus at a base pressure of 2×10^{-6} mbar. The electrode size was 9 mm² defined by shadow masking during evaporation of the metals.

4.6. Device Characterization

The current-luminance–voltage characteristics of the devices were measured using a computer-controlled Keithley 236 source measure unit for the electrical characteristics. The light output was simultaneously measured by a Si photodiode. The readings of the photodiode were converted into radiometric units by measuring the luminance at several bias voltages using a luminance meter (Minolta LS-100). This method, while being insensitive to the emission pattern of the PLED [31,32] (a Lambertian angular distribution of the emission is assumed by the luminance-meter), is a valid approach to characterize the display performance (forward-emitted light) of the device [33]. Electroluminescence (EL) spectra were recorded using a Peltier cooled charge-coupled device (CCD) camera mounted on a 0.25 m spectrograph (type Oriol Multispec), calibrated for spectral sensitivity using the same light source as mentioned above.

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