OLEDs

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Light-Induced Solubility Modulation of Polyfluorene To Enhance the Performance of OLEDs

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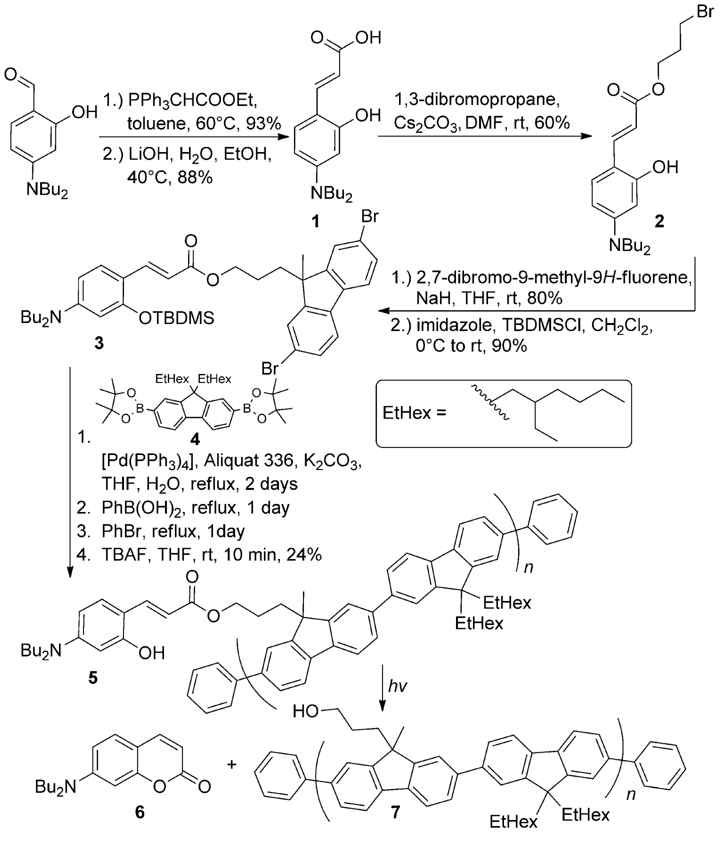
Abstract: *Liquid-phase processing is a key prerequisite for the cost-efficient fabrication of organic electronic devices. We report an approach for light-induced modulation of the solubility of π-conjugated polymers (polyfluorene) with side chains functionalized with hydroxycinnamic acid. Irradiation with light cleaves the solubilizing side chains and renders the thin films of the polyfluorene insoluble. In a proof of concept device, polyfluorenes were applied as emissive layers in OLEDs. Photoirradiation of the emission layer leads to an increase in OLED performance combined with a modulation of the solubility of the thin film. These results offer the possibility for further development in terms of manipulating the solubility and emissive parameters of an important class of functional materials.*

Over the last few decades, organic light-emitting diodes (OLEDs) have attracted great interest as a result of their promising potential as next-generation lighting sources.[1–4] However, to benefit from the advantages offered by OLEDs compared to the established inorganic semiconductor based technology, new techniques for fabricating large areas on low-cost substrates are needed.[5,6] In this context, high-throughput printing processes play a key role. Up to now, the most efficient OLEDs comprise multiple layers, and fabrication is normally achieved by vacuum deposition of small molecules. The fabrication of consecutive layers from solution is a challenge, as each deposited layer has to be resistant to the solvent used for subsequent layers.[7] However, solution-phase processing is the key prerequisite for printing. Some strategies have been developed to overcome the limitations associated with the solution-phase processing of multiple layers. Most rely on the transformation of soluble precursors, either by light or thermal treatment, to induce cross-linking[8–10] or cleavage of solubilizing side chains.[11–14] In addition, high spatial resolution of these processes is critical to realize more-sophisticated device architectures, such as pixelated OLED displays. This is mostly achieved by photolithography-like techniques to create spatial resolution.[3,15,16]



Scheme 1. Synthesis of polyfluorene **5**.

Initial studies by Jullien and co-workers showed that substituted *o*-hydroxycinnamates can be used as light-responsive groups for the release of alcohols.[17,18] Herein, we report dibutylamino-substituted *o*-hydroxycinnamates as light-responsive groups for modulating the solubility of polyfluorenes.[19] Substitution with dibutylamino groups enhances the

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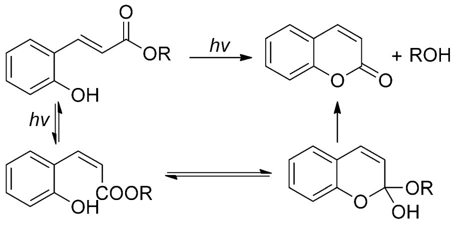
solubility of the *o*-hydroxycinnamate and allows the solubility of the conjugated polymer to be modulated when cleaved by an external trigger.[20] The cinnamate group was linked to the conjugated backbone by a similar strategy as that presented by Holdcroft and co-workers, which yielded the benign alcohol after cleavage.[21] A polyfluorene copolymer was prepared from a functionalized monomer building block with the installed cleavable group to investigate light-induced solubility modulation by one-photon processes in thin films. Furthermore, this concept of solubility modulation was investigated for its application in solution phase processed OLEDs. The synthesized fluorene copolymer was used as the emitting layer in an OLED with a simple stack architecture. Irradiation of the spin-coated emitting layer caused total insolubility in common organic solvents along with an almost tenfold improvement of the OLED performance.

The synthesis of monomer **3** (Scheme 1) started from commercially available 4-(dibutylamino)salicylaldehyde, which was first converted by a Wittig reaction into a *trans*-cinnamic acid ester. Lithium hydroxide mediated hydrolysis yielded free cinnamic acid **1**, which was selectively alkylated using 1,3-dibromopropane. Cinnamic acid ester **2** was coupled to 2,7-dibromo-9-methyl-9*H*-fluorene, and the hydroxy group was converted into its silyl ether to give **3** prior to polymerization. This step was necessary, as otherwise, palladium-catalyzed formation of coumarin occurred during polymerization. Monomer **3** was coupled with bis-borylated fluorene monomer **4** under Suzuki conditions to yield fluorene copolymer **5** in 24% yield after deprotection with tetrabutylammonium fluoride (TBAF). The number average molecular mass of **5** (by gel permeation chromatography versus polystyrene standards after precipitation form acetone) was 11.0 kg mol^{-1} (polydispersity index (PDI) = 2.00, $n = 12$ repeating units) and is in accordance with the effective conjugation length of polyfluorenes.[22,23] Although conventional Suzuki polymerizations are generally limited to polymers with number average molecular masses of several 10000 g mol^{-1}, higher number average molecular masses can primarily be reached using the Yamamoto polymerization (M_n => 200000 g mol^{-1}).[19,24]

Light-induced isomerization of the double bond of cinnamates is well-documented.[25,26] In the presence of an *ortho*-hydroxy group, *trans* to *cis* isomerization leads to the irreversible formation of coumarin with water or an alcohol leaving group (Scheme 2).[27,28] The formation of the coumarin generates a strongly emissive species at $\lambda = 440$ nm which allows easy monitoring of the reaction progress, as shown by Jullien and co-workers, through detecting the increasing emission of coumarin.[17] Comparative tests of the fluorescence intensity of hydroxycinnamic acid and coumarin confirmed these observations (see the Supporting Information).

The photolysis of monomer **3** without the *tert*-butyldimethylsilyl (TBDMS) protecting group was investigated at $\lambda = 350$ nm in dichloromethane by HPLC-MS. Here, both coumarin **6** ($R_t = 6.75$ min) and the corresponding fluorene alcohol ($R_t = 2.65$ min) were identified. The obtained retention times R_t were in accordance with those of the separately synthesized reference materials. In an initial experiment, hydroxycinnamate-functionalized polymer **5** was dissolved in chloroform and the sample was irradiated at $\lambda = 350$ nm. After distinct time intervals, the fluorescence intensity was detected at $\lambda = 440$ nm (see the Supporting Information). The time course of the reaction shows an increase in the fluorescence intensity, thus indicating that coumarin formation also takes place at the polymer. On the basis of the promising results in solution, the light-induced *trans* to *cis* isomerization was investigated in the solid state. Thus, spin-coated films of **5** on glass substrates were irradiated under inert conditions at $\lambda = 365$ nm (LEDENGIN power LED, home-built setup). The progress of the reaction was monitored by optical spectroscopy. An increase in the emission intensity clearly shows the ongoing photolysis along with the



Scheme 2. Mechanism of the light-induced formation of coumarin.

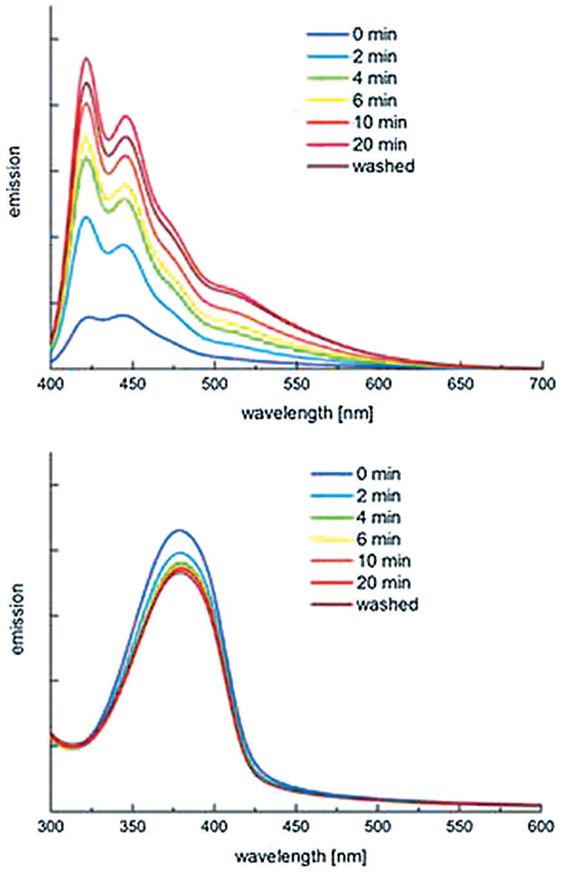


Figure 1. Time-dependent emission (top) and absorption spectra (bottom) of polyfluorene **5** on a glass substrate after irradiation at $\lambda = 365$ nm and after washing with toluene.

formation of coumarin **6**, whereas only a slight decrease is observed in the absorption spectra (Figure 1). The slight decrease in the absorption is presumable related to the lower extinction coefficient of coumarin **6** compared to that of *o*-hydroxycinnamate (see the Supporting Information). The emission and absorption spectra show a superposition of the spectra of polyfluorene and coumarin. No change in the absorption was observed after washing the irradiated films with organic solvents (THF, dichloromethane, chloroform, toluene, diethyl ether, ethyl acetate, ethanol).

This last observation shows the insolubility of the polymer and of the entrapped coumarin within the polymer film after irradiation. If non-irradiated films were washed with one of the solvents mentioned above, a complete decrease in the absorbance was observed, thus indicating complete dissolution. The slight decrease in the emission of the irradiated films is presumably caused by partial extraction of coumarin from the upper layers through washing. The formation of coumarin clearly indicates efficient photolysis in the solid state. Since at the same time no changes in the absorption spectra were observed, photochemical degradation of the material can be ruled out. Light-induced modulation of the solubility could also be used in microstructuring by photolithography (Figure 2). Thermal treatment of thin films of **5** showed an identical optical behavior as irradiated films.

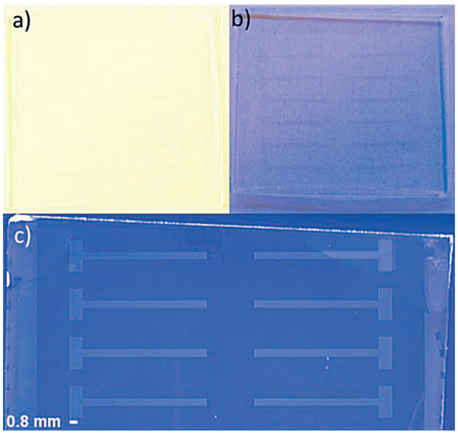


Figure 2. Photolithography of **5** on a glass substrate using a shadow mask and illuminated a) under ambient light on a white background, b) from the side at $\lambda = 365$ nm on a white background, and c) from underneath at $\lambda = 365$ nm.

Thermally treated films (200 °C, 10 min) of **5** showed resistance to common organic solvents but were not completely insoluble, which would require longer heating or higher temperatures.

To demonstrate the functionality of this novel concept we tested **5** as an emissive layer in an OLED. As proof of principle, OLEDs with simple stack architectures consisting of ITO/PEDOT:PSS/emission layer (EML)/Ca/Al were fabricated. The solution-processed emission layer was irradiated for 10 min at $\lambda = 365$ nm under an inert atmosphere. As a reference, a spin-coated film on a glass substrate was irradiated under identical conditions and analyzed by optical spectroscopy. Washing the irradiated reference substrate with toluene resulted in no change in the absorption, thus indicating insolubility of the material. This finding indicates that the applied conditions are sufficient to modulate the solubility of the thin film. All the OLED data are summarized in Table 1 and Figure 3. Full functionality of the solution-processed OLEDs was obtained, with relatively low current efficiencies of about 0.004 cd A^{-1} and luminance of 15 cd m^{-2} before irradiation. OLEDs which had been irradiated showed an almost tenfold increase in efficiency, with a maximum of 0.03 cd A^{-1} and a brighter luminance of 52 cd m^{-2}. The luminance of the irradiated samples increases by a similar factor as the fluorescence upon irradiation of thin films. As

Table 1: OLED data based on **5** as an emitting layer.

Device	L_{max}[c] [cd m^{-2}]	V [V]	CE_{max}[d] [cd A^{-1}]	V [V]	CE_{10}[e] [Cd a^{-1}]	V [V]	V_{on}[f] [V]
1[a]	15.0	16.0	0.004	15.0	0.003	15.6	13.6
2[b]	52.0	15.2	0.03	14.1	0.03	13.5	11.8

[a] EML without UV irradiation. [b] EML with UV irradiation. [c] Maximum luminance. [d] Maximum current efficiency. [e] Current efficiency at a luminance of 10 cd m^{-2}. [f] Threshold voltage at 1 cd m^{-2}.

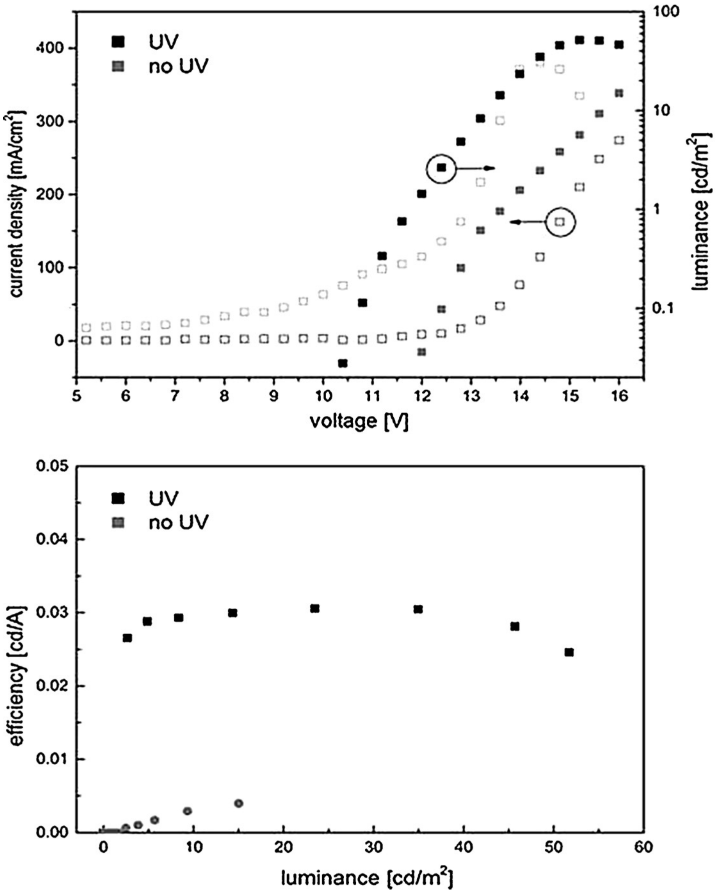


Figure 3. OLED data based on polymer **5** as an emitting layer before (gray) and after irradiation (black) at $\lambda = 365$ nm for 10 min under inert conditions.

a consequence of the simple stack architecture of the OLED, no optimization of the layer thickness, and irradiation under non-clean room conditions, the luminance of the OLEDs is situated in the lower region for reported OLEDs comprised of polyfluorene as the emitting layer.[29–31] Since the electroluminescence spectra of OLEDs show no difference before and after irradiation, we presume that the formed coumarin works as a dopant in the film and thus contributes to the increased efficiency.

In subsequent work it is necessary to investigate the detailed relationship between coumarin formation and increased efficiency. Initial studies towards solubility modulation with two-photon absorption also showed promising results, thereby paving the way for high spatial resolution (see the Supporting Information) and are part of upcoming investigations. The presented concept will also be used for the construction of highly efficient multilayer systems and its applicability in other components investigated (OPV, OFETs, etc.).

The reported synthesis of polyfluorenes having side chains functionalized with hydroxycinnamic acid generates solution-processable polymers with electronic and chemical properties that can be tuned by irradiation with light or heat. These materials represent a new approach to solution-processed multilayer OLEDs with a disposable solubilizing side chain. Polyfluorene **5** displays, in prototypical OLEDs, a tenfold increase in performance as well as cleavage of the solubilizing side chains after irradiation. The ability to modulate the solubility by two-photon processes opens a wide range of diverse applications, where microstructuring is mandatory, including microchip-based sensors.

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