Abstract

Organic light-emitting diodes (OLEDs) are one of the most active research fields in industry, as well as in university groups. Over the last decade a lot of progress has been made; the first consumer products were released on the market.

The major advantages of OLEDs over competing technologies, such as liquid crystals, in the application field of displays are the self emittance of the materials, resulting in brilliant colours, a large viewing angle and high power efficiency. The interest in OLEDs for solid-state lighting grew over the last years, as life-time and power efficiency increased steadily.

OLEDs are on the threshold of mass application in both fields: display technology and lighting. To this date, however, it is not clear whether OLEDs will meet all requirements from industry, especially those regarding production costs and life-time.

The general structure of an OLED consists of one (or more) organic layer(s) sandwiched between two electrodes through one of which the generated light is emitted. Usually indium-tin-oxide (ITO) is used as transparent anode, as its relatively high work-function and the transparency in the visible region of the spectrum make it well suited. Typical cathode materials are metals with low work-function such as barium or calcium.

OLED-Research is traditionally divided into two different approaches: vacuum-sublimation of small molecules and solution processing of polymers. Both bear advantages and disadvantages.

The major advantage of small molecule OLEDs is the possibility to build up defined layer structures by successive evaporation of different materials. Advanced device architectures with individually optimised layers can be realised. Among other problems the relatively high costs are a major disadvantage. Furthermore, large area-coatings are difficult to realise and require even more costly equipment.

Cost efficiency, high through-put (e.g. for roll-to-roll processes) and relatively simple realisation of large-area coatings are the main advantages of solution-processed OLEDs. Here, pixilation for display application is difficult, as is the realisation of multi-layer structures.

In the group of Prof. Meerholz a class of cross-linkable organic semi-conductors has been developed, that allow for pixilation and the fabrication of multi-layer structures. They provide the necessary prerequisite for a “best of two worlds” – the semi-conductors can be applied from solution and be made insoluble in film: advanced device architectures based on solution processing can be achieved.

For such a procedure a (photo-) cross-linkable group in the semiconductor is needed, which has to fulfil certain requirements. Little volume shrinkage upon crosslinking is desired to avoid mechanical stress and micro cracks in the layers. The electrical and optical properties of the organic semiconductor shall neither be influenced negatively by the introduction of the cross-linkable group nor by the cross-linking process itself. The oxetane group meets all the above requirements; oxetane can be polymerised cationically or radically. Photoinitiators as well as one-electron oxidants or acids can be utilised to initiate the cross-linking process. One major advantage of the oxetane group is that it is inert in basic conditions, in which the transition-metal catalysed coupling reactions for the polymerisation of organic semi-conductors are carried out. A convergent synthesis is thus possible to implement oxetanes in

“state-of-the-art” polymers. These oxetane-functionalised organic semi-conductors are the tool for the fabrication of advanced device architectures – comparable to those applied in small molecule OLEDs.

The goal of this work was, therefore, to realise advanced device architectures, which are known from small molecule OLEDs, in solution processed devices. The devices are thereby optimised regarding operating voltage, efficiency and life-time. Cross-linkable emitter materials furthermore allow for the fabrication of OLEDs with “mixed” emission colours and finally of a white emitting device.

OLEDs are usually optimised regarding drive voltage, power efficiency and life time.

Drive voltage and efficiency are influenced by the injection barriers for the charge carriers (“electrons” and “holes”). To optimise both, therefore, the charge-carrier injection needed to be improved. This is demonstrated using the well known and already optimised PPV-polymer Super Yellow. The tools for this optimisation were a cross-linkable hole-conducting material for improved hole-injection and, for improved electron-injection, a cathode with low work function (alkali fluoride). With an optimised combination of improved hole- and electron-injection the charge-carrier balance in the Super Yellow device is improved, resulting in reduced operating voltages, improved (power) efficiency and substantially prolonged life-time.

Often poly-(ethylene 3,4-dioxy-thiophene) (PEDOT) is used as hole-injection layer in OLEDs. PEDOT is usually doped with poly-styrene-sulphonic acid (HPSS); the mixture exhibits a very high conductivity. Hole injection is improved by application of PEDOT, the properties of PEDOT are far better to control than those of ITO. It has, however, been speculated that PEDOT – among other difficulties, such as ions diffusing into the emissive layer with unknown effects – might be one of the limiting factors for the life-time in OLEDs. To overcome these deficiencies, alternative hole-injection has been tested in a blue emitting OLED. The PEDOT layer is successfully replaced by a cross-linked hole-conducting layer. Upon operation warming of devices is usually observed, which is simulated by a heat-treatment step. Devices with hole-conducting layer were resistant to heat-treatment, where devices on PEDOT did show efficiency loss.

In earlier work general mechanisms for the cross-linking of oxetanes have been developed:

In photosensitised cross-linking the semiconductors serve as sensitizer for the added photoacid. Upon UV-illumination a photo-electron transfer (PET) from the sensitizer to the photoacid takes place. The formed radical of the photoacid decomposes to give a phenyl radical that can react with the radical cation of the semiconductor in two different ways. The first reaction (**A**) is a combination of a radical and a radical cation, after which a proton is released, which can start the oxetane polymerisation. The second reaction (**B**) is “unproductive”: a CH-abstraction on the semiconductor takes place, the radical cation of the semiconductor remains in the film.

Oxidative cross-linking of oxetane-functionalised semiconductors is initiated by adding a strong single-electron oxidant. The semiconductor is oxidised to the radical cation. In a concerted reaction, in which two radical cations and (at least) two oxetane groups participate, the polymerisation of oxetanes is initiated.

During both possible mechanisms for cross-linking, photosensitised and oxidative, radical cations are generated and do partially react during the cross-linking process. As radical cations effectively quench fluorescence, fluorescence spectroscopy was used in this work to quantify the amount of radical cations. The goal of these investigations is further understanding of the mechanisms and the dependencies on different parameters, such as the oxidation potential or the glass-transition temperatures of the functionalised organic semiconductors. Different methods for the removal of radical cations in cross-linked films can be evaluated using fluorescence spectroscopy.

With the above results, fluorescence spectroscopy was used to estimate the amount of radical cations formed upon cross-linking in different organic semi-conductors. These radical cations constitute intrinsic doping sites. In hole-conductors this intrinsic doping leads to reduced operating voltages, as demonstrated in hole-only devices. In cross-linked emitter layers the removal of radical cations is crucial for the recovery of the efficiency of the device. In blue emitting devices both chemical and thermal removing of radical cations is successfully demonstrated.

Based on the results obtained from the fluorescence experiments the fabrication of devices with specific doping in the hole-conducting layer could be carried out.

Two different hole-conductors are investigated in combination with a blue emitter. The influence of different doping levels in the hole-conducting layers can be summarised as follows: with increasing doping level the operating voltage decreases. Secondly, the efficiency decreases with increasing doping level, which is an undesired effect. The problems with reduced efficiency are circumvented by the introduction of an additional, undoped hole-conducting layer between the doped hole-conducting layer and the emitter. The efficiency is improved in comparison to a single layer device of the same blue emitter by up to 20%.

To reduce production costs in industrial applications the application of lower quality, cheaper ITO-layers is desired. Usually thick PEDOT layer are used to make lower quality ITO-layer applicable. The doped hole-conducting layers introduced allow for the fabrication of blue emitting OLEDs with “thick” doped hole-conducting layers (up to 200 nm). The application of low-cost ITO becomes feasible.

A further possibility to initiate the cross-linking of oxetanes is adding acid. But instead of adding the acid to the semiconductor, the acidity of PEDOT is used to initiate the cross-linking process. This new method of cross-linking oxetane-functionalised semiconductors is presented in this work for the first time. No additives to the semiconductor are necessary for this so called “acidic” crosslinking method. The dependence of this new method on various parameters, such as temperature of heat-treatment, composition and layer-thickness of PEDOT is investigated for two different polymeric hole-conducting materials.

In hole-only devices the applicability of this new method is demonstrated, the hole-conducting properties of the materials are nearly unaffected by the cross-linking procedure. Hole-conducting interlayers – cross-linked acidic from PEDOT – have been successfully implemented in two-layer blue emitting OLEDs. With the polymer investigated tripled efficiency and ten times prolonged life-times were achieved, compared to a single-layer blue-only device. Optimisation of layer thickness of both, the hole-conductor and the blue emitting polymer, while keeping the overall thickness constant, has proven a powerful tool for increasing efficiency and life-time. A structure containing 40 nm HTL and 60 nm blue emitter is ideal regarding high efficiency and good life-time. In the system investigated, maximum efficiencies of up to 4 Cd/A is reached; the extrapolated life-time at 100 Cd/m^2 reaches 10 000 h, meeting the required values for industrial application.

The novel cross-linking method paved the way for surface-directed phase separation (SDPS). With this new preparation method phase-separation of two materials, one of which contains oxetane moieties, is gained. The mixture of the two materials is applied onto an acidic surface e.g. PEDOT, upon heat-treatment cross-linking of the oxetane-functionalised component is initiated from the PEDOT interface, the second component is driven to the surface. Thus phase-separation takes place resulting in a layer structure with the cross-linked material below the non cross-linkable material. In other words: “apply the mix, get a layer structure”! The concept is successfully applied to blends of two sets of a cross-linkable hole-conductor and a non cross-linkable emitter material.

The advanced layer structures investigated in this work are applied to the fabrication of OLEDs with new colours. By layering blue-emitting and red-emitting polymers on top of each other, magenta-coloured OLEDs were realised.

Thorough investigations of different architectures containing these emitting materials gave evidence to the mechanisms responsible for the generation of the mixed emission colour. Charge-carrier trapping in the red-emitting layer on the dye moieties, as well as energy-transfer from the blue emitting layer to the red dye in the red emitting layer are most probably the main mechanisms. Depending on – among other factors – the relative layer thickness of both polymer layers mixed colours ranging from blue over magenta to red can be realised.

Red-emitting devices from this series exhibited a substantially improved efficiency compared to only red devices. Obviously red emission originating from energy transfer from an exciton in e.g. a blue emitting layer resulted in higher efficiencies compared to emission from an exciton generated in the red emitting layer itself. This tendency was also observed in magenta coloured devices.

Devices with a blue layer on top of red show colour-stability for operating voltages ranging from 4 to 10 V, whereas devices with inverted layer sequence exhibited a colour-shift with increasing operating voltage. This behaviour was attributed to different trap depth for holes and electrons in the red emitting layer. Inverted-layer devices might be applied in fields, where colour-tunability is desired, for example as indicators for different temperatures.

The concept of layering cross-linkable emitter materials has been successfully applied to the fabrication of a white-emitting OLED. White emission in an OLED with a layer-structure of two different emitter materials can be obtained from combining complementary colours. From the different colour-combinations possible, turquoise on top of red was chosen for the high efficiency expected for this architecture.

The turquoise is obtained by mixing a green and a blue emitter in different proportions. In a device consisting of a 30 nm red layer below an 80 nm layer with a 50:1 blue to green ratio colour-stable white emission was obtained. The efficiency of this device is 3.5 Cd/A. The parameters of the emission colour can be summarised as follows: CIE-coordinates: $x = 0.3$, $y = 0.35$, CRI = 72 and CT = 6600 K; these characteristics are close to the values required for solid-state lighting and thus form a promising basis for future experiments.