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Modern Trends in Organic Light-Emitting Devices (OLEDs)

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Summary. Synthesis of crosslinkable small and large organic molecules having OLED properties will be presented. Three strategies for the construction of multilayer devices will be described. In the first case small, well-defined OLED-molecules are functionalized with oxetanes as crosslinker. The second case deals with polymers having OLED active units in the main chain and pendant crosslinkers and finally it was shown that styrene polymers with pendant OLED functions and crosslinkers can be applied for the construction of such multilayer and multicolour devices.

Keywords. Organic light-emitting diodes; Hole transport; Oxetane; Photo crosslinking; Triarylamines.

Introduction

The display market is a fast growing area, driven by developments in the field of portable electronic devices like cellular phones, digital cameras, *etc*. OLED-technology may become a strong competitor for the liquid crystal display (LCD) technology in the near future. Today, simple OLED displays are already integrated in shavers (Philips), car stereos (Pioneer), and cellular phones (Samsung). Although this technology is young compared to the inorganic light emitting devices, mainly based on semiconduction, the quality of OLEDs can compete with them in many cases [1]. The conservative assumption is, that the OLED market climbs the 1000 million USD line soon and will increase almost exponentially the next few years [2].

OLEDs *versus* LCD

OLEDs have several advantages over LC displays.

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OLEDs:

- will need less space and are better suited for large displays;
- show self emission, high resolution, higher scan rate, and better color reproduction;
- show a higher luminous efficiency, a higher flexibility, and a maximum viewing angle;
- can be manufactured at lower production costs;

but they need improvement for long term stability.

A typical one-layer OLED consists of a metal cathode (*e.g*. Ca, Al, Ba), an organic semiconducting layer which allows for transportation of electrons and holes, and an anode, *e.g*. ITO (a transparent alloy of indium oxide and tin oxide) based upon a transparent carrier material (glass or a flexible polymer) (see Fig. 1). Above a certain voltage electrons are induced into the organic layer resulting in a radical anion. This electron moves through the layer by a hopping process from one

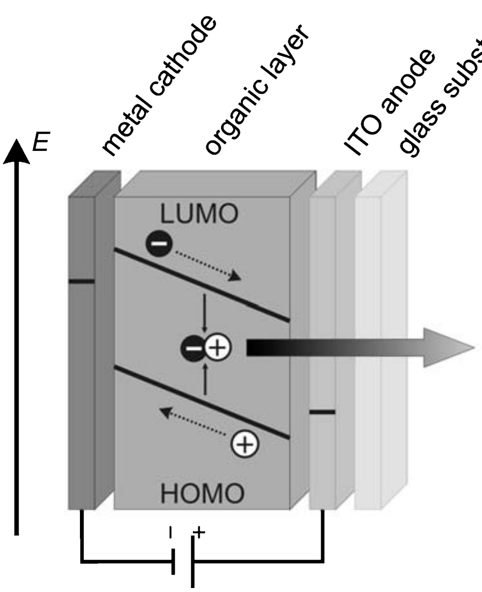

Fig. 1. Scheme of a one-layer OLED

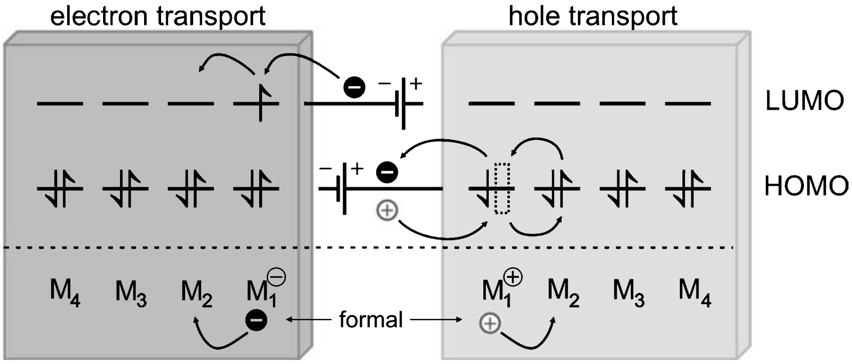

Fig. 2. Charge transport in OLEDs *via* hopping processes without mass transport

molecule to the other until it meets an ‘electronical hole’ - a defect electron formed by the abstraction of an electron at the anode. This abstraction leads to a radical cation which is neutralized again by receiving an electron from the neighbour molecule, thus drifting in the direction of the cathode (see Fig. 2).

If two of these opposite charges meet, they recombine to form an excited state called exciton, which relaxes from the excited to the ground state resulting in the emission of light. This process is called electroluminescence and is the basic principle of organic as well as inorganic light emitting devices.

The known problems of such devices are:

- the process of charge injection into the organic layer
- the transport of electrons and holes through the organic layer
- the danger of exciton quenching if the recombination takes place in the vicinity of the electrodes
- a passing of charges through the layer from electrode to electrode without recombination (dark current).

A possible answer to this list of problems might be a multilayered device structure.

Multi-Layer Devices

A multi-layer device consists of an emission layer (EL) sandwiched between hole and electron transport layers (HTL and ETL respectively) (see Fig. 3). This general structure serves three main purposes: (1) it facilitates charge carrier injection by reducing the respective injection barriers; (2) the recombination of electrons and holes in the emissive layer is enhanced due to accumulation of charges in the EL

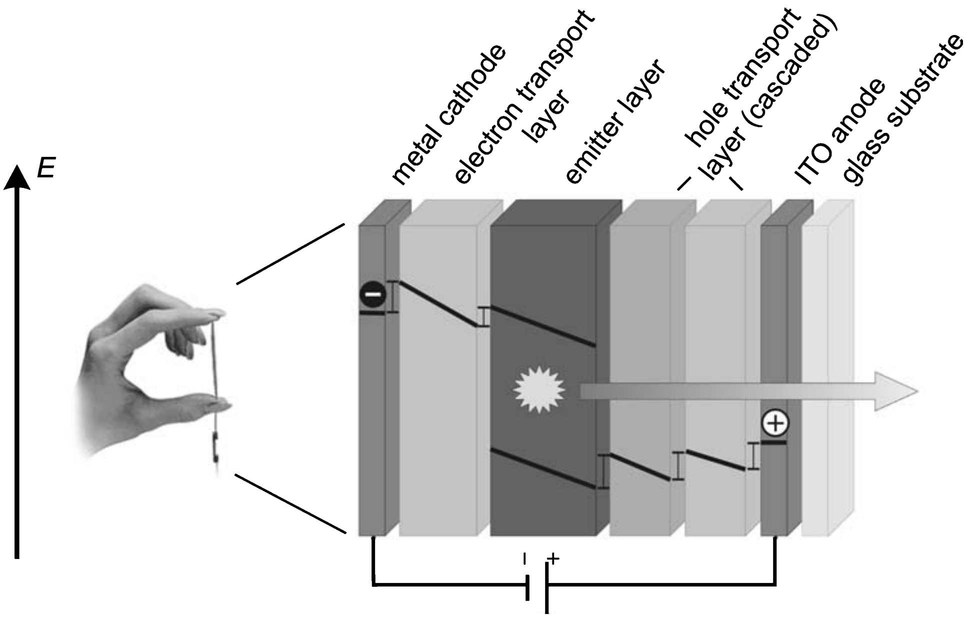

Fig. 3. Scheme of a multi-layer OLED with electron transport layer, emitting layer, and two energetically cascaded hole transport layers

(charge carriers are blocked by the opposite transport layer – the HTL is a barrier for electrons and the ETL for holes); (3) the recombination area is shifted towards the middle of the device and thus quenching of the excitons at the electrodes is avoided.

In the following passage some basics on materials used in OLEDs are given [3–5]. The colour of the emitted light can be tuned by the molecular structure of the organic emissive material (see Fig. 4). Typical emitters for different colours can either be well-defined low molecular compounds such as *DPVBI* (4,4′-bis(2,2-diphenyl-ethene-1-yl)diphenyl) für blue emission, *Alq3* (tris(8-oxychinolinato)aluminum)

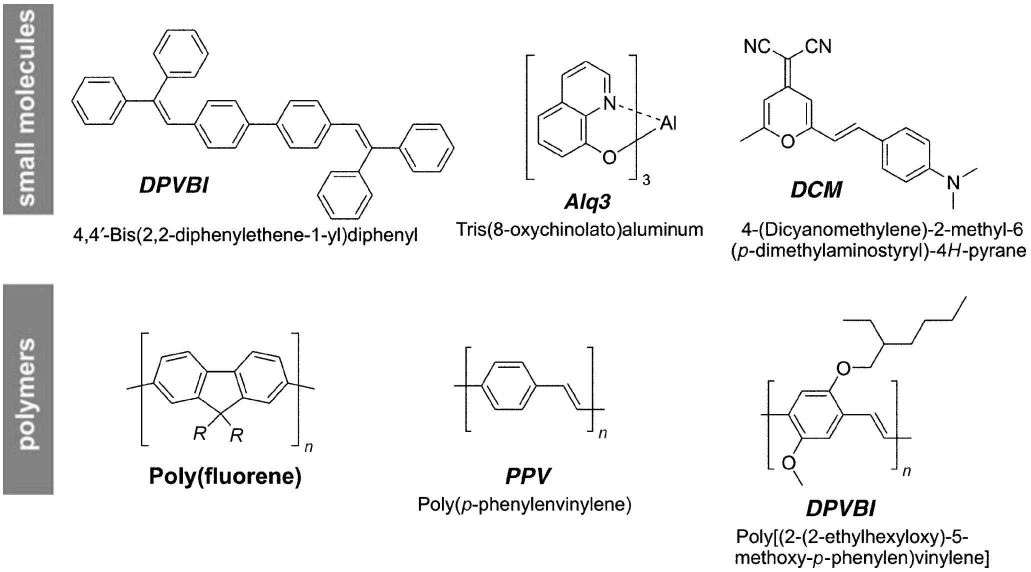

Fig. 4. Chemical structures of various emitting materials used in OLEDs

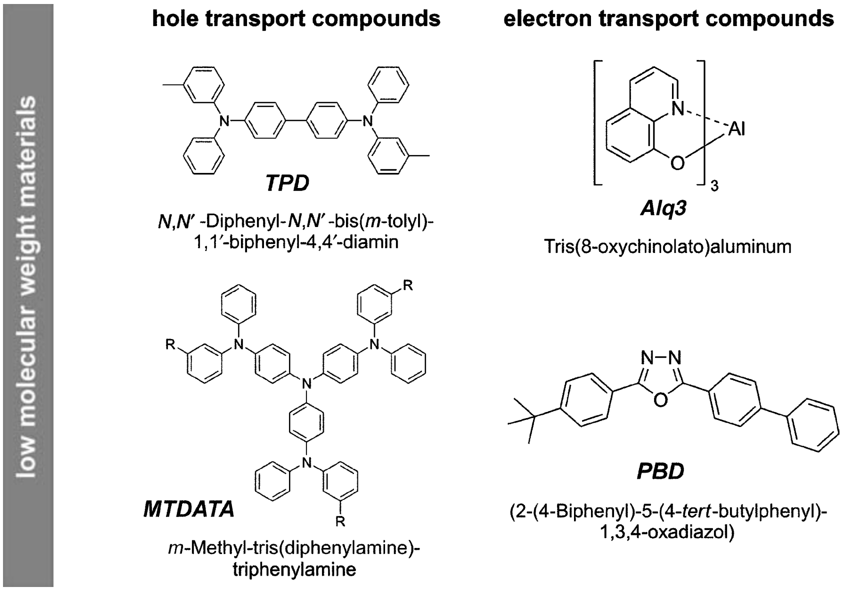

Fig. 5. Various hole transport and electron transport materials used in OLEDs

for green emission [6], and *DCM* (4-(dicyanomethylene)-2-methyl-6-(*p*-dimethylaminostyryl)-4*H*-pyrane) for red emission, or polymers such as polyfluorenes (blue) [7], *PPV* (poly(*p*-phenylenvinylene)) (green) [8], and *MEH-PPV* (poly[(2-(2-ethylhexyloxy)-5-methoxy-*p*-phenylen)vinylene]) (orange) [9].

Typical hole transporters are materials based on the triarylamine motive like *TPD* (*N*,*N*′-bis(3-methylphenyl)-*N*,*N*′-diphenylbenzidine) or *MTDATA* (*m*-methyltris(diphenylamine)triphenylamin), while compounds like *Alq3* and *PBD* (2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole) are able to transport electrons especially well (see Fig. 5).

Polymers *versus* Low Molecular Weight Compounds

OLED materials can be divided by their molar mass into low and high molecular weight compounds. Polymeric materials have many advantages over low molecular weight compounds. They show good processability and wide area and also flexible applications are possible. They possess excellent film forming properties, do not crystallize, and allow for low cost manufacturing techniques from solution like spin coating. The design of new structures is possible with a great variety of synthetic methods.

Technologies for Preparation of Multi-Layer Devices

Devices can be built up either *via* vacuum sublimation or from solutions. Both strategies have advantages and disadvantages. The charm of sublimation methods is the additional final purification step and the fact that multiple layers can be constructed without serious problems. However, sublimation is limited to vaporisable low molecular weight materials and can only be applied to compounds which endure thermal stress without decomposition. This technology is relatively expensive and can only be applied for smaller devices which then however exhibit high quality. For polymeric materials and large-area devices preparation from solution is more suitable and also less expensive than sublimation. However, multi-layer preparation from solution is far from trivial. It is of crucial importance that previously deposited layers are absolutely resistant against the solvent used to deposit the subsequent layer(s).

The simplest strategy to conquer this problem is the application of OLED compounds dissolved in orthogonal solvent systems for each individual layer. In most cases this strategy fails because of solubility problems of the desired OLED materials. Alternatively, one can change the polarity/solubility of the material after the layer preparation, as in case of the transformation of a sulfonium precursor of *PPV* (soluble) into *PPV* (insoluble). Yet the most elegant strategy is the application of precursors containing polymerizable groups which are converted into an insoluble network by an additional crosslinking step [4].

Concepts for the Preparation of Multi-Layer Devices by Crosslinking

The first concept deals with low molecular weight compounds consisting of an OLED functionality and attached polymerizable units (in this case photopolymerizable

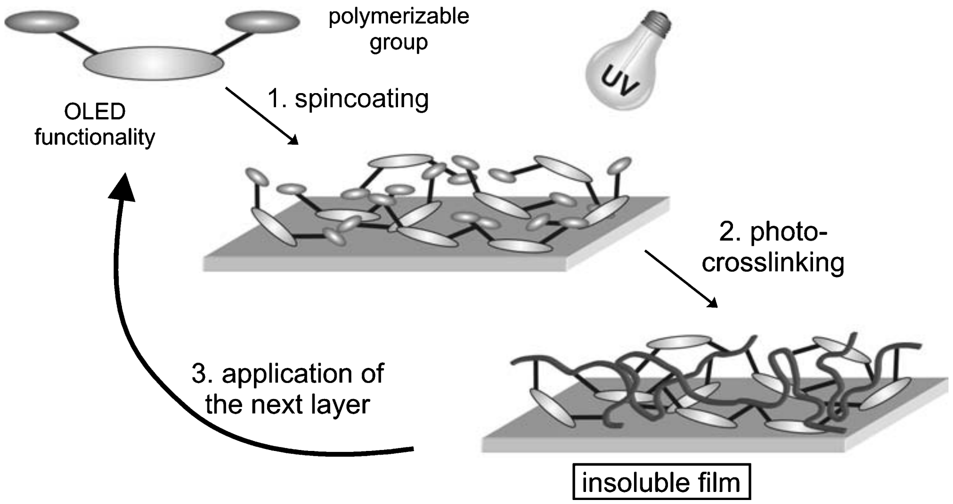

Fig. 6. Preparation of a multi-layer OLED by spincoating and photocrosslinking

oxetane functionalities). Those compounds can be spincoated and finally be transferred into an insoluble polymeric network by irradiation with ultraviolet light (see Fig. 6) [10–12].

Alternatively, one can use polymers containing OLED active units. Such polymers can have the 'diluted' or 'undiluted' OLED functionalities located in the main chain and pendant polymerizable units (*e.g.* oxetanes) attached to the backbone ('dilution' with non-OLED active units) [11, 13, 14]. The third concept deals with common polymers, like polystyrene, with OLED and crosslinking functions in the side chains [15–17]. The processing sequence to build multi-layer devices with polymeric materials is the same as in the case of low molecular weight materials. Figure 7 summarizes these concepts.

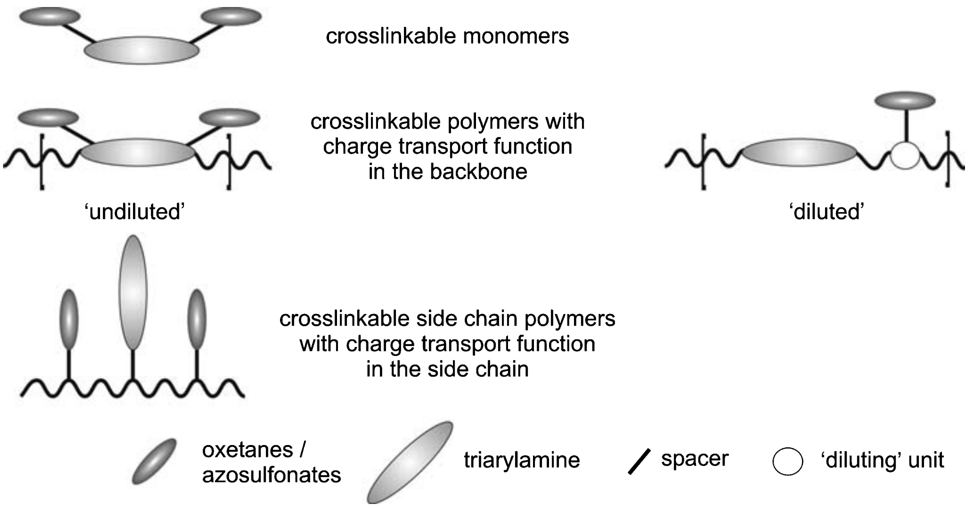

Fig. 7. Concepts for the preparation of multi-layer devices by crosslinking

Examples of Crosslinkable Hole Transporters

Figure 8 shows two examples of hole transport materials based on *TPD* used for model studies in which the OLED units are bridged by a fluorenyl unit either open or cyclic. The advantage of the cycle over the open compound is its higher glass transition temperature making the material more stable. By variation of R_1 and R_2 (phenyl, naphthyl, *etc.*) the glass transition temperature Tg of both compounds can be varied between 147 and 202°C [10, 11]. It should not be a serious problem to modify these compounds and to introduce pendant oxetane (compare Fig. 10) or other crosslinkable functions such as azosulfonates (compare Fig. 14).

The main synthetic method used to build up such hole transport materials by palladium-catalyzed amination reaction became known as *Hartwig-Buchwald* reaction (Fig. 9) [18, 19] and has mostly replaced the formerly used *Ullmann* coupling with its drastic reaction conditions.

The characteristics of this reaction are high yield (around 90%), mild reaction conditions from room temperature to around 100°C, and the fact that even chlorinated aromatics can be applied.

Figure 10 shows some examples of crosslinkable low molecular weight compounds.

The connecting functions between aromatic amines and the oxetane groups (circled in Fig. 10) are either alkyl, phenol, or benzylalcohol groups and influence

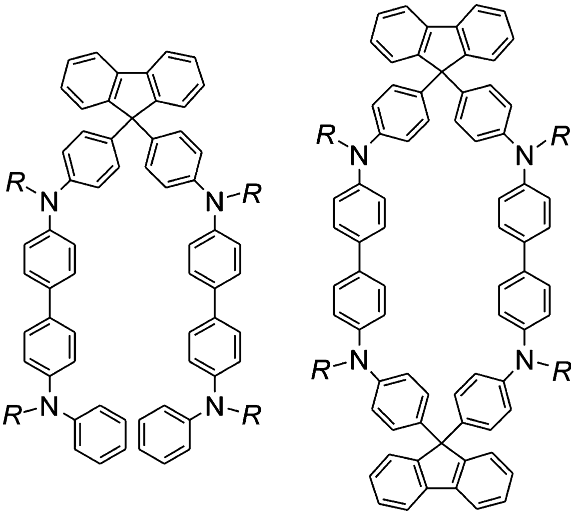

Fig. 8. Hole transport materials bridged by fluorenyl units

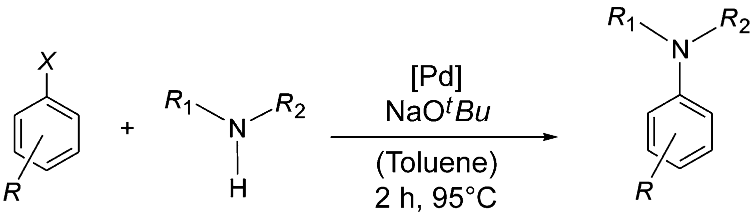

Fig. 9. The *Hartwig-Buchwald* reaction

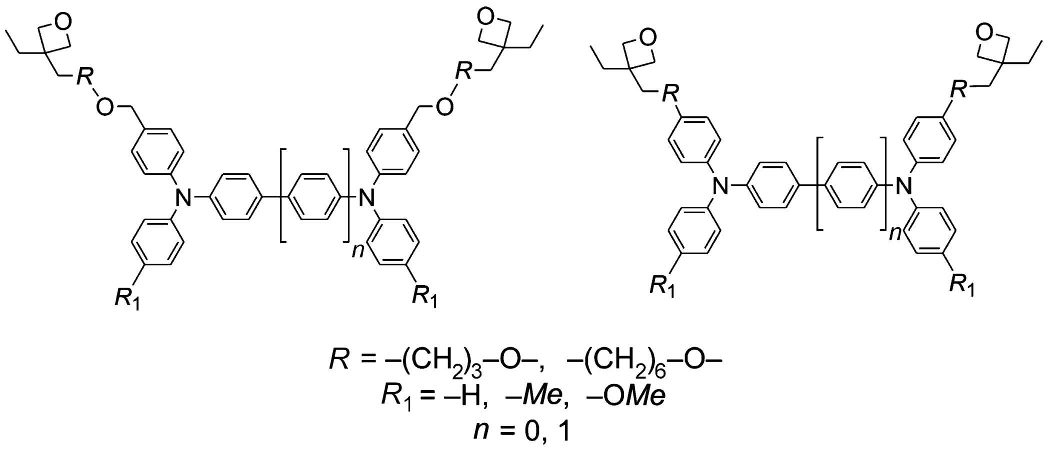

Fig. 10. Monomeric hole transporters with crosslinkable oxetane units

the oxidation potential – an important characteristics for energetically cascaded layers. All of them are stable enough under the reaction conditions of the *Hartwig-Buchwald* coupling and for display applications. They are applied *via* spincoating followed by photocrosslinking [12].

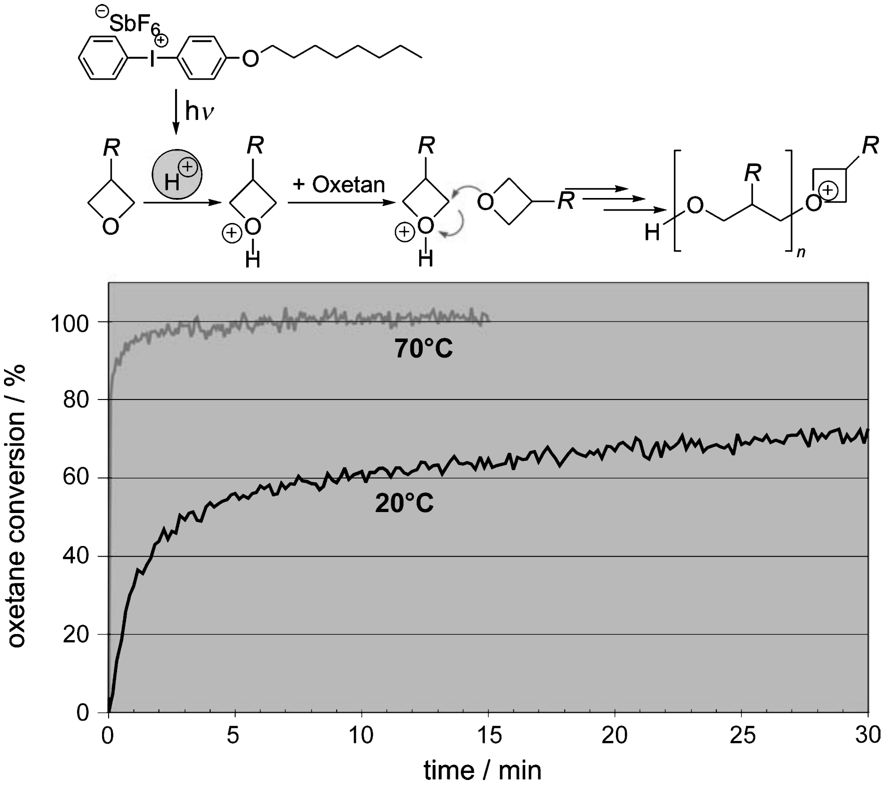

Fig. 11. UV induced ring-opening photopolymerization of oxetanes and realtime FT-IR measurements to observe the kinetics of this reaction

The crosslinking process is initiated with sulfonium or iodonium salts which produce protons on UV-irradiation (so-called photoacids). The protons are initiators for the cationic ring-opening polymerization of the oxetanes. The reaction is completed in a few minutes as one can see from realtime FT-IR measurements (see Fig. 11) and leaves the layer insoluble. The quality of the crosslinked layer can be proven by solvent treatment of the film and UV spectroscopy. In case of complete insolubility the layer should not change its absorption after several washing steps. All investigated oxetane bearing hole transporters (monomers as well as polymers) can be rendered totally insoluble by photoinduced crosslinking.

Alternatively to oxetanes, pendant azosulfonate functions can be used for crosslinking purposes [20, 21]. Those functions can be decomposed by UV-light. In this case crosslinking is possible without the need of additional photoinitiators. Therefore, contamination of the layers with additives can be avoided.

From cyclic voltammetry studies one can obtain valuable information about energy levels of the molecules. They are also useful to estimate the chemical stability of the charge-transporting radical ions. These measurements showed that all synthesized monomeric and polymeric hole conductors exhibit fully reversible redox processes and are stable under operational OLED conditions.

The last and most important characterisation step of OLED materials are complete test devices. A typical example is shown in Fig. 12 in which a PEDOT system, a monolayer with a synthesized crosslinked monomer and a cascade of three layers of crosslinked hole transport compounds are compared.

Typical examples of polymers with OLED active units in the main chain and their synthesis are shown in Fig. 13. They are synthesized *via Hartwig-Buchwald* reaction using a 'molecular construction kit' with variable monomers B_2. Further

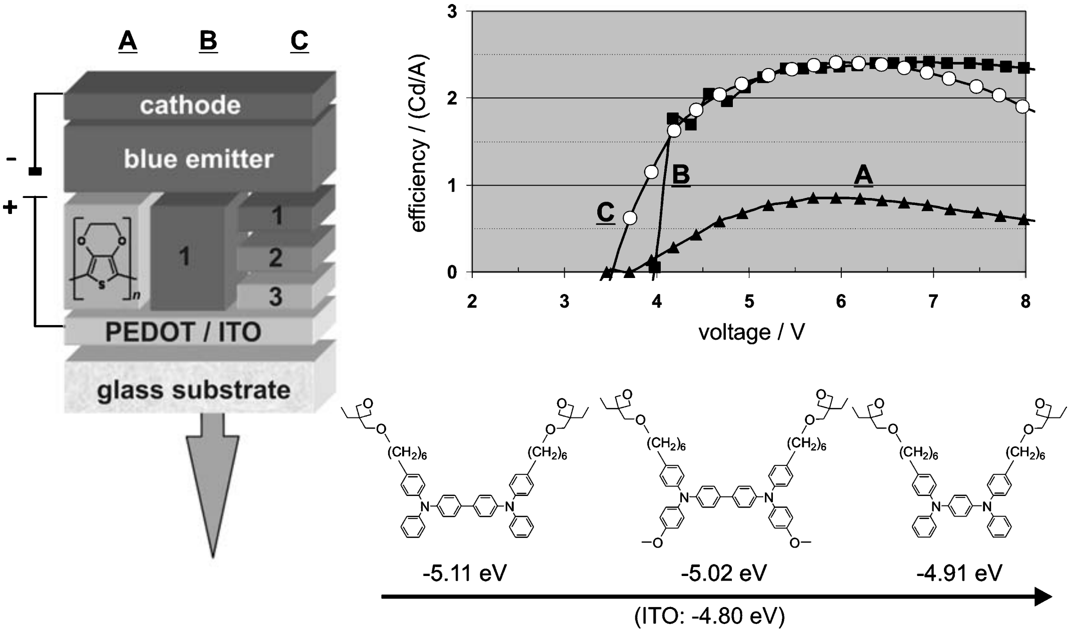

Fig. 12. Characterization of different OLEDs built up with crosslinkable hole transport monomers

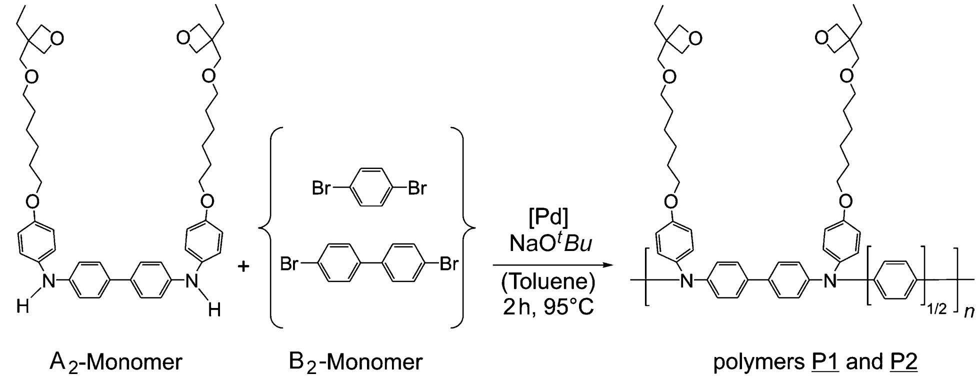

Fig. 13. Crosslinkable hole transport polymers with the OLED active *TPD* unit in the backbone

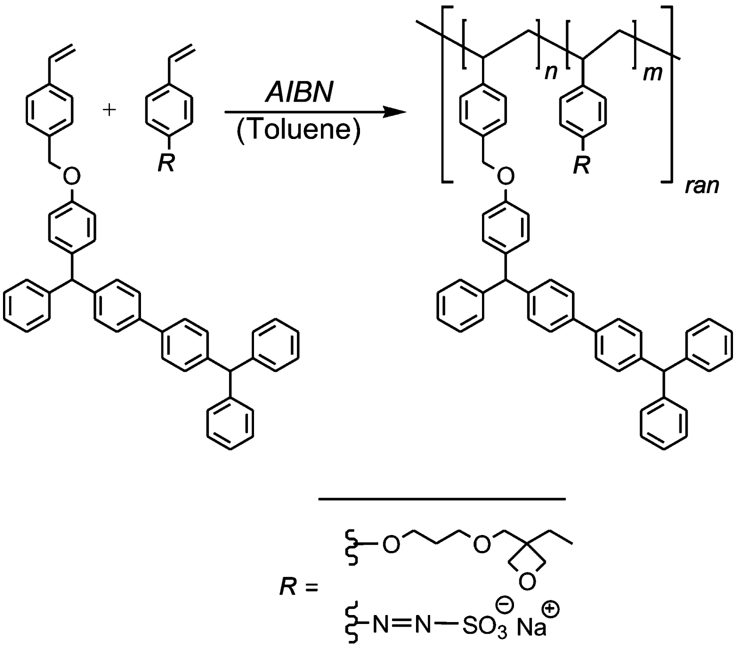

Fig. 14. Crosslinkable hole transport polymers with OLED functionalities in the side chains; the crosslinking units can either be oxetanes or azosulfonates

possible B_2 compounds include fluorenyl or thiophene units. Different polymers vary in oxidation potential and hole transporting ability [13].

Figure 14 shows some monomers (of the third concept) on the basis of styrene with pendant hole transport functions and crosslinkable oxetane units. These monomers can be polymerized in various ratios *via* free radical polymerization using a radical starter like *AIBN* [15, 21].

The advantage over the main-chain polymers described before is that no transition metals are required as catalysts in the polymer synthesis, since such metals are known to act as quenching sites in the devices and so reduce their quality and lifetime.

Light Emitting Polymers with Defined Conjugation Length

It was one of our aims to synthesize soluble polymeric emitters with controlled conjugation length. Light emitting polymers like polyfluorenes, polythiophenes, or poly-*p*-phenylenes normally suffer from poor solubility and their optical properties

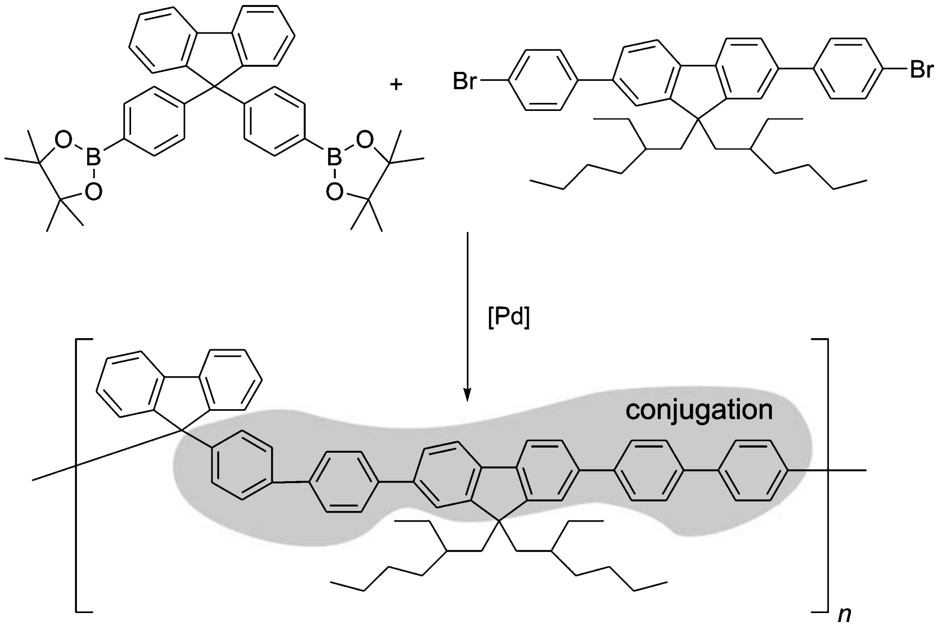

Fig. 15. Light emitting polymers with defined conjugation length *via Suzuki* reaction

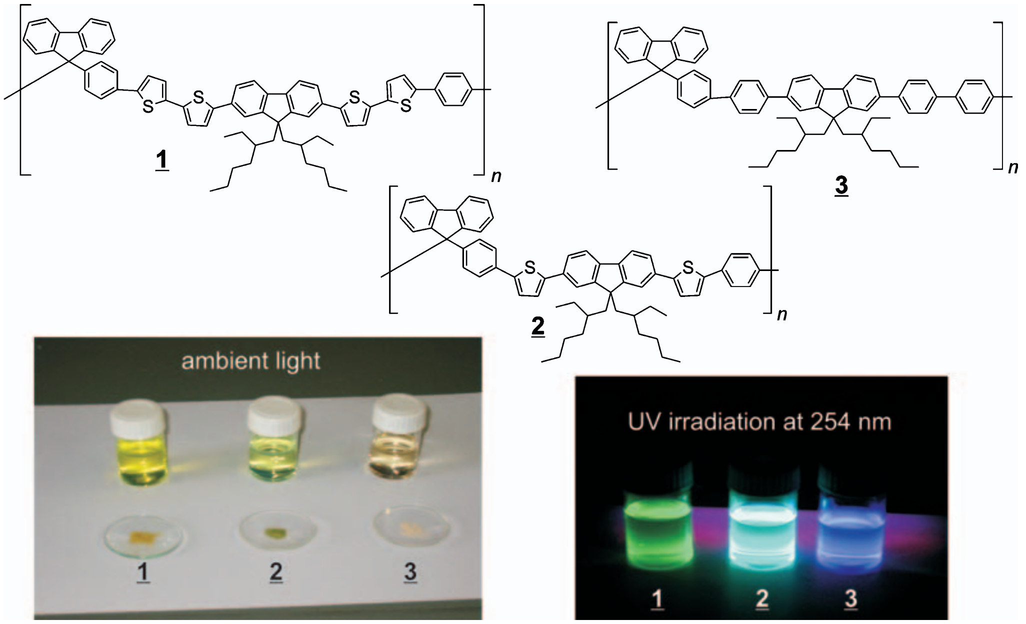

Fig. 16. Light emitting polymers with defined conjugation length and their appearance under ambient and UV light

are strongly dependent on their molar masses. This mass dependency can be overcome if units of certain length are bridged by non-conjugated units thus defining the conjugation length in the polymers. While the spiro-fluorenyl units applied in our system interrupt the conjugation, the conjugated fluorenyles bear alkyl chains to improve the solubility of the polymers dramatically, making them applicable to solution based processing methods. Such compounds were synthesized *via Suzuki*-coupling as shown in Fig. 15 [22, 23].

The optical properties can be tuned by the type of conjugated units (thiophene, phenylene, or fluorene) and their number between two spiro-connected fluorenes (sp^3-C). Some examples of such polymers and their fluorescence behaviour are depicted in Fig. 16 [22].

Full Colour Capability

The main target of OLED technology is the field of RGB (red, green, blue) displays. For wet-chemical fabrications of RGB devices current research efforts are directed towards adaption of printing techniques such as screen and inkjet printing. Recently we have described a suitable alternative system to obtain multicoloured

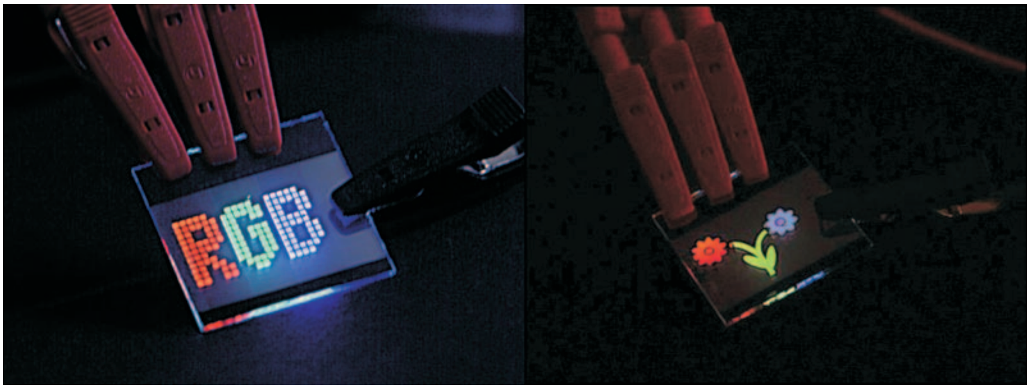

Fig. 17. RGB devices designed *via* spincoating and crosslinking [24]

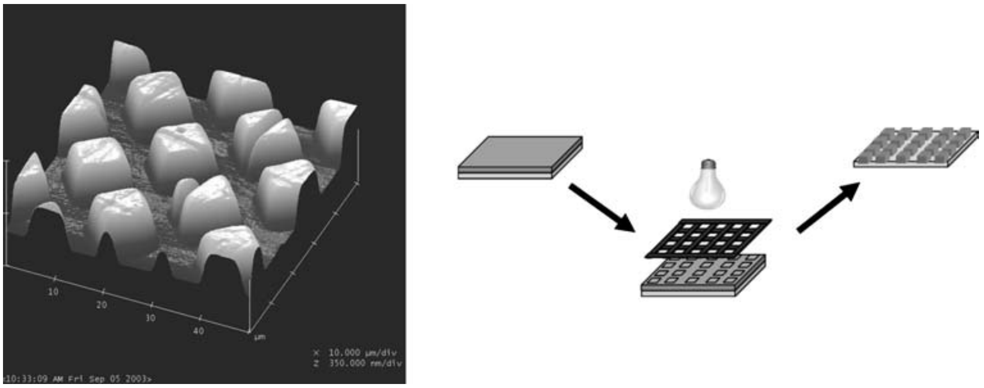

Fig. 18. Lithography test setup using TEM grids (5 µm structures) and an AFM image of a patterned hole transport material [25]

OLEDs based on spin coating and photo-crosslinking. The three different polymeric materials were subsequently spincoated onto the entire substrate, and crosslinked/patterned by UV illumination. Then the excess polymer was removed from the non-illuminated areas and the next colour was applied. A final curing step removed residues from the initiation process (see Fig. 17) [24].

A very simple method we developed to test the lithographic resolutions of photopatternable materials is to use TEM grids as contact shadow masks. AFM investigations of crosslinked layers structured by using this method show that the grid is reproduced accurately into the material (Fig. 18) [25].

Conclusion

In this presentation we have discussed general concepts of designing mono- and multilayer OLEDs. Most efficient devices were obtained using a multilayer approach with several crosslinked hole transport layers in addition to emitting and charge blocking layers. This approach makes small molecules and polymers applicable to solution processing. Soluble materials become insoluble *via* photocuring of pendant oxetane or azosulfonate functions. The resulting films are of high quality with a very smooth surface. Crosslinking takes place in short time and under moderate conditions. Shrinkage of the layer is negligible (<5%) and the crosslinking process has no influence on the optical and electronic properties of the layer. Also we were able to build up polymeric light emitting materials with tunable optical behaviour by defined conjugation lengths.

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