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## Liquid Crystals

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## Preliminary communication

# Multilayer light emitting diodes based on columnar discotics

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Columnar discotics were used as the hole transporting layer in single layer, two layer and three layer light emitting diodes because of the unusually large hole mobility of such materials. The observations are that the onset fields are small compared with most devices using non-discotic hole transporting layers, that these values are strongly reduced with increasing number of layers, that the orientation of the columns along the layer film normal causes a further decrease of the onset voltage and finally that the quantum efficiencies increase significantly as the number of layers is increased.

The most simple organic light emitting diode [1–4] consists of just one layer located between the hole and the electron injecting electrodes. The active organic material has in this case to provide several functions simultaneously. It has to act as transport layer for holes as well as for electrons and it has to control the recombination process giving rise to the emission of light. Optimization procedures aimed at increasing the quantum efficiency and at reducing the onset field for emission are severely limited in such one layer devices. Multilayer devices are possible solutions [5–8]. Three layer devices consist, for instance, of a hole and an electron transport layer separated by an emission layer. Two layer diodes have also been considered in the literature.

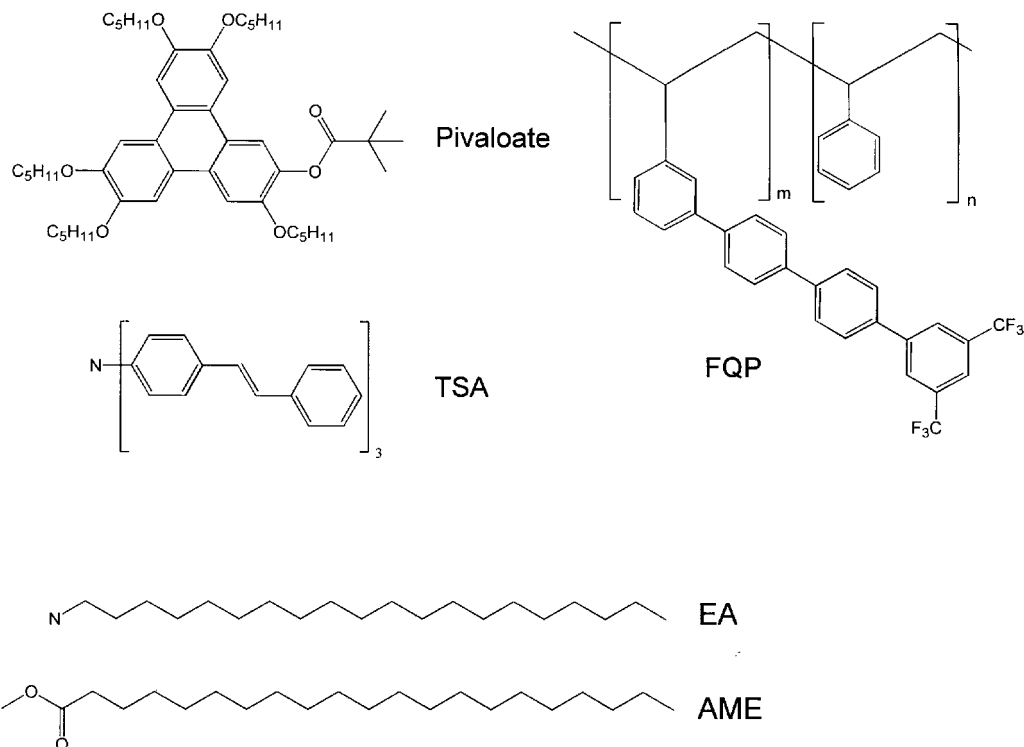
Considerable efforts are currently devoted to the development of novel materials for the transport layers. Electron transport materials have received special attention [5, 9, 10]. Of current interest, however, are also hole transport materials with high charge carrier mobilities. Conjugated polymers or amorphous polymers acting as host material usually display charge carrier mobilities in the range of  $10^{-5}$ – $10^{-6}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> [11]. Columnar discotic systems, on the other hand, have been found to display unusually large hole mobilities of up to  $10^{-2}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> [12–15]. This makes these systems prime candidates for application not only in the area of photoconductivity, but also for LEDs. The mobility was furthermore found to depend strongly on the degree of

order within the columnar phase [12, 14]. We reported recently that the highly ordered columnar plastic phase displays an unusually large charge carrier mobility [12]. In addition, such systems have the advantage that all properties including the carrier mobility are anisotropic; this offers additional degrees of freedom as far as optimization is concerned. We have recently demonstrated the potential use of low molar mass and polymer columnar discotics for applications in the area of light emitting diodes [16–18].

It was therefore decided to investigate multilayer diodes containing discotics as hole conducting materials. We prepared diodes composed of one, two and three layers. Single layers were prepared by spin-coating from pure discotics, as well as from discotics with the chromophore TSA (see the scheme) as active material. The preparation of two and three layer devices required special care because of the low molar mass of the discotics. This gives rise to high solubilities of the discotics in many solvents and to poor mechanical properties of the discotic layer. Bilayer devices were obtained using the Langmuir–Blodgett technique [19, 20] to deposit the chromophore layers on top of the discotic film. A hole blocking layer composed of a quarterphenyl-side group polymer was transferred in the same way. The monolayer technique enabled us to organize the target molecules in a well defined way within the emitting layers.

We will now describe the results obtained for devices composed of the compounds shown in the scheme. The

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triphenylene compound (pivaloate) displays a columnar discotic plastic (Col<sub>hp</sub>) phase [12]; no crystallization takes place on cooling since the discotic phase is frozen in at the glass transition. The synthesis and properties of the tertiary amine TSA have been described previously [21]. The eicosylamine (EA) was used in order to improve the stability of TSA monolayers for the two and three layer devices. The hole blocking layer was prepared from a mixture of the fluorinated quarter-phenyl copolymer (FQP) with arachidic acid methyl ester (AME) for the same reason.

Figure 1 displays the photoluminescence spectra of the single, two and three layer devices with the chromophore TSA controlling the emission properties. All systems are characterized by an emission maximum at about 450 nm; it is apparent that the emission spectra originate in all cases from the TSA [22]. Similar results are obtained for the electroluminescence spectra of all devices containing TSA (figure 2).

The diode characteristics of the single, two and three layer devices (in the positive branch) differ significantly. We observe a strong reduction of the onset fields with increasing number of layers (figure 3). The threshold field decreases from  $5 \times 10^5 \text{ V cm}^{-1}$  for a single layer to  $2.5 \times 10^5 \text{ V cm}^{-1}$  for the bilayer and finally to  $2 \times 10^5 \text{ V cm}^{-1}$  for the three layer device. An interesting observation is that the onset voltage may be modified

by heating the pure discotic layer into the isotropic state and subsequently cooling it into the columnar phase. Figure 4 shows that this results in a further decrease of the onset voltage to  $1.5 \times 10^5 \text{ V cm}^{-1}$ . This is one order of magnitude lower than the values usually reported for multilayer devices [23, 24]. The reason for this reduction obviously is that the columns orient parallel to the substrate normal. We have already shown previously that this kind of reorientation leads to a significantly decreased onset voltage [16].

The expectation is, of course, that the introduction of additional layers should not only decrease the threshold fields, but also that the use of a hole blocking layer should lead to a significant increase of the quantum efficiencies and thus of the intensity of the emitted light for a given current density. It is for this reason that we compared the integrated intensities emitted by diodes with different numbers of layers for wavelengths in the range between 300 and 700 nm. We considered for this purpose a single layer device with 33 wt% of TSA and a three layer device with an oriented discotic. For a current density of  $15.695 \text{ mA cm}^{-2}$  an increase of more than one order of magnitude for the three layer device was found despite the fact that the three layer device contained just two monolayers of TSA.

The general conclusion is that discotic materials may be used with great advantages in LEDs. Discotic hole

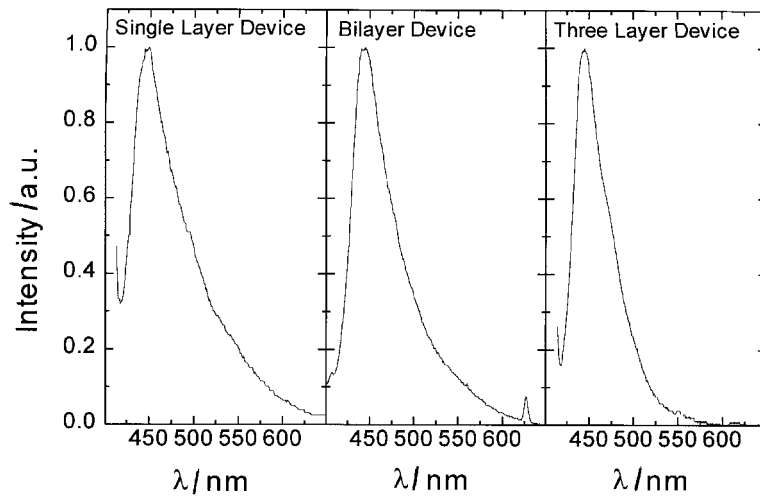


Figure 1. Fluorescence spectra for single, two and three layer devices.

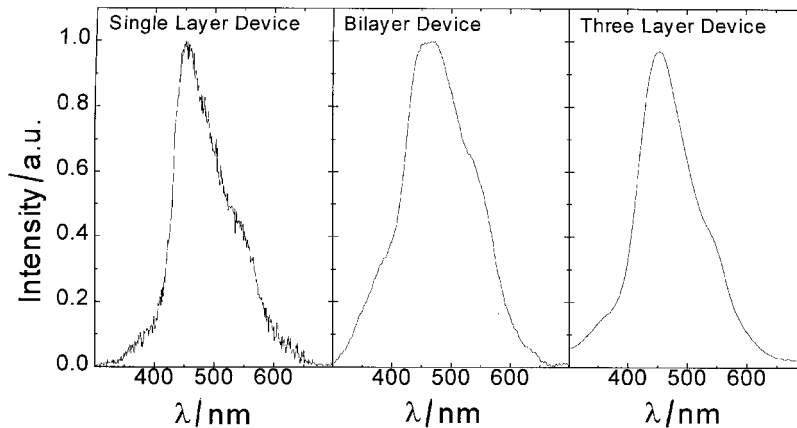


Figure 2. Electroluminescence spectra for single, two and three layer devices.

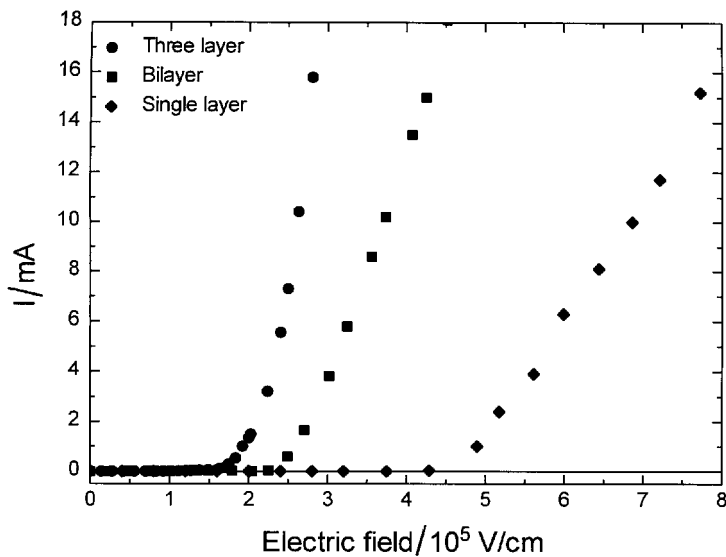


Figure 3. Diode characteristics for single, two and three layer devices with spin-coated discotic layers.

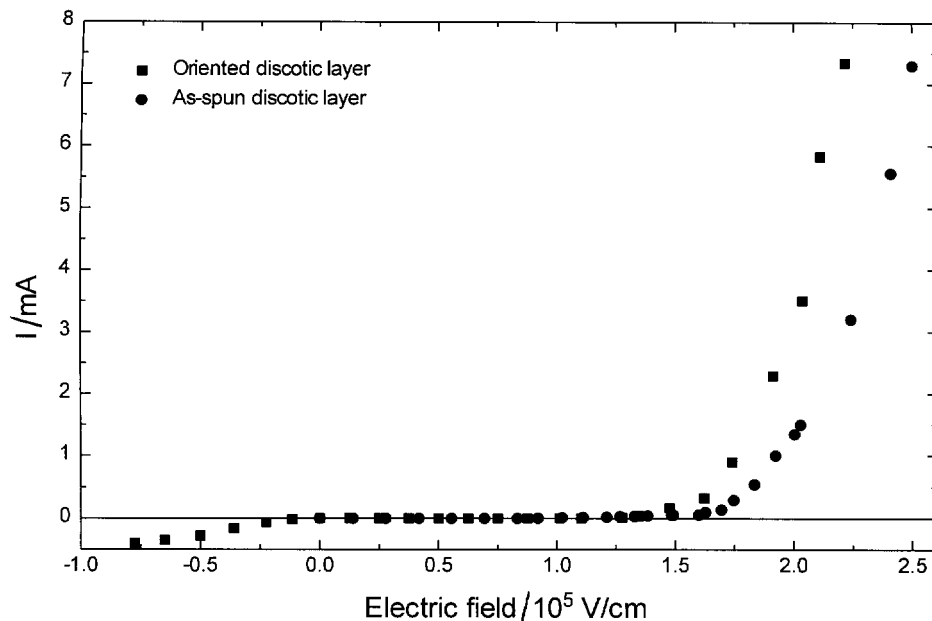


Figure 4. Diode characteristics for three layer devices with a spin-coated discotic layer and with a quenched discotic layer.

transport layers decrease the threshold field significantly, and we expect fast responses due to the unusually large charge carrier mobility along the columnar axis. It is possible to prepare well defined multilayer structures, even with low molecular mass liquid crystalline compounds, using the Langmuir–Blodgett technique. The quantum efficiencies may be significantly increased by the introduction of a hole blocking material such as FQP.

The following experimental details are now given. Films for single layer devices were prepared by spin-coating (2000 rpm) of solutions of 1 wt % of the discotic compound in chloroform on ITO substrates. Discotic/chromophore systems were made of 1 wt % discotic/TSA (2:1) in chloroform. The second and third layers were transferred by the Langmuir–Blodgett technique described in the following. The water used as subphase for monolayer preparation was taken from a Milli-Q-System (Millipore). Spreading solutions were made by mixing appropriate volumes of the following chloroform solutions:  $1 \times 10^{-3}$  M TSA,  $1 \times 10^{-3}$  M EA,  $1 \times 10^{-3}$  M AME and 1 wt % FQP. Monolayers were prepared using a rectangular PTFE trough. In order to prepare the chromophoric monolayer, a mixture of the TSA and EA solutions, ratio 1:5, was spread and the monolayer was compressed to  $40 \text{ mN m}^{-1}$ . For the transfer of the third layer a mixture of FQP and AME solutions, ratio 1:2, was spread and the monolayer compressed to  $20 \text{ mN m}^{-1}$ . The monolayers of TSA and FQP were transferred using the Langmuir–Blodgett technique of vertical dipping and withdrawal so that on each cycle two monolayers were transferred. A thin aluminium

layer (typically 150 nm) was vacuum evaporated ( $P < 10^{-6}$  mbar) on top of all devices.

The thickness of the active layers was determined using the surface profiler Dektak<sup>3</sup>ST from Veeco Instruments. The absorption spectra were recorded with a Perkin Elmer type Lambda 9 spectrometer. Photoluminescence spectra were recorded with a Shimadzu type 1509 spectrometer with an excitation wavelength of 404 nm. Electroluminescence spectra were also recorded with a Shimadzu type 1509 spectrometer.

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