Novel Aromatic Amines for Photoconductor and Organic Electronic Applications

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Abstract

Aromatic amines are frequently used as hole conductors in copiers and laser printers. In the last decade there has been increasing interest to extend the use of aromatic amines to organic light emitting diodes (OLEDs) as well as to organic field-effect transistors (OFETs) developed for printable organic electronics. In this contribution star-shaped aromatic amines which form stable amorphous phases are introduced. Such materials are often called molecular glasses. We have used molecular glasses with triphenylamine, triphenylbenzene and fluorene units as blue emitters and hole blocking materials in OLEDs. The layer thickness of the hole transport and emission layer and the hole blocking layer were optimized in a combinatorial approach which leads to pure blue emitting OLEDs with color coordinates of x=0.15 / y=0.15, a brightness of 400 cd/m² and an efficiency of 2 cd/A. We have also used molecular glasses with triphenylamine and carbazole units as organic semiconductors in OFETs and obtained environmentally stable transistors with mobilities up to 10^{-4} cm²/Vs.

Introduction

In copiers and laser printers aromatic amines are an integral part of the photoconductor drum. Imbedded in a polymer matrix they serve as hole conductors in the charge transport layer [1]. A number of aromatic amines used in photoconductor drums is shown in Fig. 1.
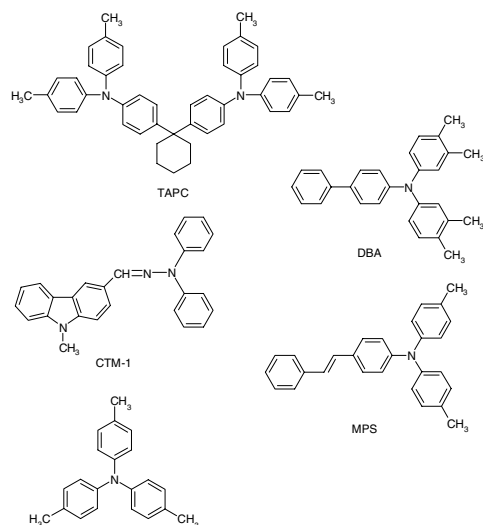

Figure 1. *Chemical structure of aromatic amines used in photoconductor drums*

The pioneering work of C. Tang and S. Van Slyke [2] on thin film organic light emitting diodes (OLEDs) has shown that aromatic amines can also be used as hole transport materials in OLEDs. In their first OLED, Tang and VanSlyke used vacuum evaporated films of the hole transporting diamine TAPC together with the electron transporting and green emitting complex 8-hydroxyquinoline aluminum (Alq₃). Since then the use of many different aromatic amines in OLEDs has been described.

Among the large number of materials reported in literature, star-shaped aromatic amines have received special interest. Molecules with a star-shaped geometry usually have a very low tendency to crystallize and for that reason are also known as molecular glasses [3-5].
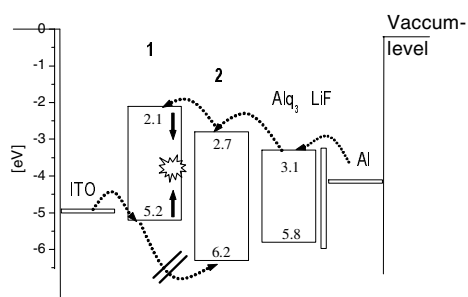
Organic Light Emitting Diodes (OLEDs)

We have prepared a number of molecular glasses from triphenylamine, triphenylbenzene and fluorene building blocks [6]. In Fig. 2 two representative molecules are shown.
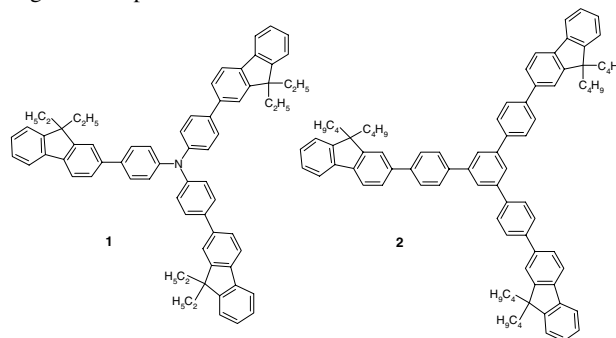

Figure 2. *Chemical structure of the two molecular glasses 1 and 2 used for the development of blue OLEDs.*

1 with a triphenylamine core and three fluorene side arms exhibits a strong blue fluorescence. The HOMO level of **1** is at -5.2 eV and the optical band gap is 3.1 eV. This makes **1** a good candidate as hole conductor and blue emitter in an OLED. The device configuration and the energy level diagram of the OLED are shown in Fig. 3. On top of the indium tin oxide electrode a thin layer of the triphenylamine glass **1** is evaporated. In order to confine the excitons in this layer and to avoid exciton migration to the Alq₃ it was necessary to introduce a hole blocking layer of the molecular glass **2**. The chemical structure of **2** is similar to **1** except that the electron donating triphenylamine core is replaced by triphenylbenzene. This leads to a much lower HOMO level at -6.2 eV and a band gap of 3.5 eV. The HOMO level offset of 1 eV between **1** and **2** makes **2** an efficient hole blocker in our device

setup (Fig. 3). On top of the blocking layer an electron transport layer of Alq_3 is evaporated followed by an lithium fluoride injection layer and an aluminum cathode.

Figure 3. Device configuration and energy level diagram

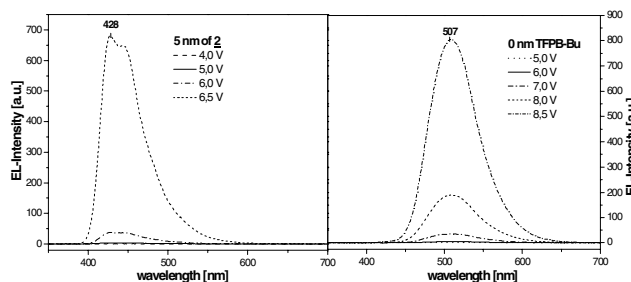## *Combinatorial device preparation*

For the variation of the different layer thicknesses we have used a combinatorial approach which allows an efficient material screening and device optimization [7]. Our setup for the combinatorial device preparation allows us to prepare 40 OLEDs under identical conditions in one experiment. The setup is shown in Fig. 4. Note that each sector consists of 4 identical OLEDs. The preparation of an internal reference sector within the same combinatorial experiment, in our case the preparation of an OLED without a hole blocking layer, is an important advantage of the method. In the upper part of the substrate (area 1) the thickness of the hole blocking layer of **2** is varied in small steps of 5 nm between 0 and 20 nm. In the lower part (area 2) the thickness of the emission layer of **1** is varied between 40 and 70 nm in 10 nm steps. For comparison a device without hole conductor is included in sector J.
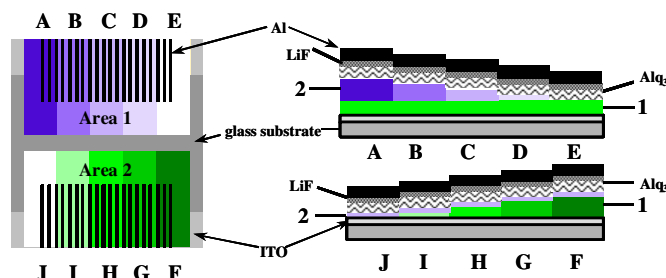
Figure 4. Schematic representation of the combinatorial library of the multi-layer OLED with two different step thickness gradients of the HBL **2** in area 1 and the HTL **1** in area 2 (Left: top view; right: side view); area 1: **1** (70 nm) / **2** (0-5-10-15-20 nm)/Alq_3 (20 nm) / LiF (1 nm); area 2: **1** (0-40-50-60-70 nm) / **2** (10 nm) / Alq_3 (20 nm) / LiF (1 nm)

The electroluminescence spectra of different OLEDs from the combinatorial device are shown in Fig. 5. In sectors A-D as well as in F-I blue electroluminescence with a maximum at 428 nm was detected. The electroluminescence (EL) spectrum is almost identical to the photoluminescence (PL) of a thin film of the emitter molecule **1**. In sector E, where no hole blocking layer was used, the EL is shifted to 507 nm, which is attributed to an Alq_3 emission. Furthermore Fig. 5 indicates that a hole blocking layer of only 5 nm thickness is enough to prevent an escaping of the holes

to the Alq_3. The CIE-coordinates of the blue devices are x = 0.15 and y = 0.15.

Figure 5. EL-spectra of OLEDs at different voltages; left sector D: ITO / **1** (70nm) / **2** (5nm) / Alq_3(20nm) / LiF / Al; right reference sector E: ITO / **1** (70nm) / Alq_3(20nm) / LiF / Al.
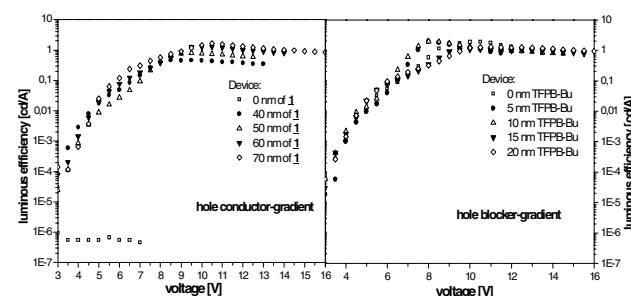
Figure 6 Voltage-luminescence characteristics; right: area 1 HBL (**2**) with a step thickness gradient from 0-20 nm; left: area 2 HTL (**1**) with a step thickness gradient from 0-70 nm.
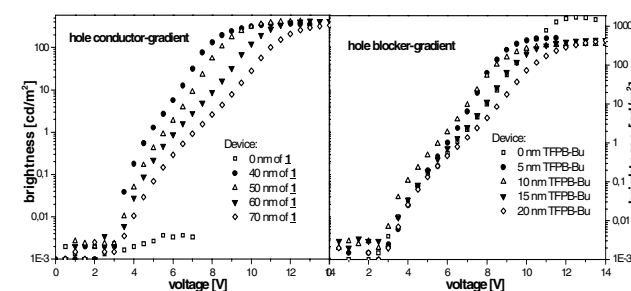
Figure 7. Electroluminescence efficiency versus voltage; right: area 1 HBL (**2**) with a step thickness gradient from 0-20 nm; left: area 2 HTL (**1**) with a step thickness gradient from 0-70 nm.

From Fig.6 it can be seen that the OLEDs have an average onset voltage at 4-4.5 V. The blue emitting devices have a typical brightness of 400 cd/m^2 at 10 V (Fig. 6, left). The green reference devices reach about 1700 cd/m^2 at 12.5 V, which is a common value for Alq_3-based OLEDs. The increase of the brightness is faster in devices with very thin hole conducting layers. But as shown in Fig. 7 the efficiency of luminescence is higher with thicker emitter layers. This can be attributed to the decreasing current density with increasing layer thickness, but keeping a similar

brightness. On the other hand Fig. 6 shows no significant correlation of the hole blocking layer thickness to the brightness, but with increasing the thickness of the hole blocking layer the luminescence efficiency decreases by factor of 2 from 2 cd/A to 1 cd/A (Fig 7). Note that the blue OLEDs with thin hole blocking layers between 5 and 10 nm are slightly more efficient than the Alq_3-based reference device.
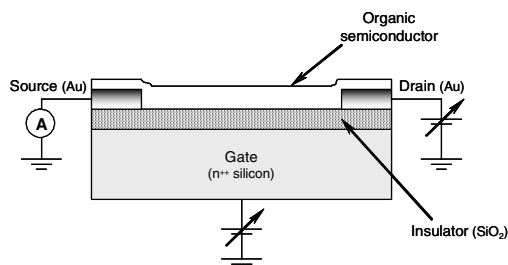
Organic Field-Effect Transistors (OFETs)

A second area in which aromatic amines have achieved a lot of interest is organic electronics [8]. The basic idea of organic electronics is to replace silicon based integrated circuits by simple circuits made from organic semiconductors which can be manufactured by cheap printing techniques. For this application OFETs are key devices.

We have synthesized a number of novel triphenylamine based star-shaped molecules and used them as p-type organic semiconductor in solution-processed organic field-effect transistors [6]. Two of the materials are shown in Fig. 8.
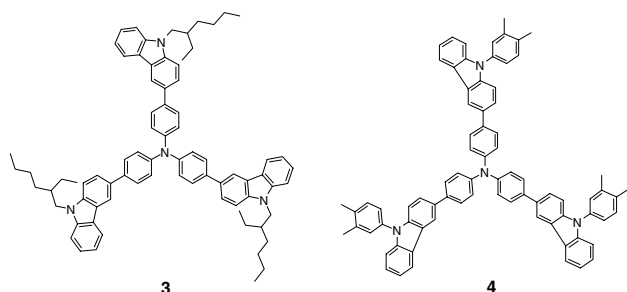
Figure 8. Chemical structue of the molecular glasses **3** and **4** used in OFETs

By using N- alkylated and N-phenylated carbazole units as side arms of the molecular glasses with a triphenylamine core we obtained electrochemically stable materials with a high solubility in common organic solvents and good film-forming properties. **3** and **4** were obtained in excellent purity by using medium pressure liquid chromatography (MPLC). This is an important issue as high purity is a basic requirement for organic materials used as semiconductors in electronic devices.


**Figure 9**. Schematic of an organic field-effect transistor

The new compounds were tested in solution processed organic field-effect transistors. The OFET devices were prepared on heavily doped n^{++} silicon wafers as gate contact on top of which an insulating layer of silicon dioxide was thermally grown. Gold was evaporated and photolithographically patterned to form the source and drain contacts [9]. The devices were completed by deposition of the star-shaped molecules by spin-coating from toluene or methylene chloride solution. The electrical measurements were carried out either in air or in vacuum (10^{-4} Torr) using a Hewlett-Packard semiconductor parameter analyzer Agilent 4155C. The transistors had a ring configuration with a channel length of 40 μm and a channel width of 1000 μm.

The transistor architecture is shown in Figure 9 [6]. The drain current was measured as function of the gate bias (forward sweep from 0 V to –20 V / backward sweep from –20 V to 0 V). The transistors were tested with two fixed drain potentials of –2 V and –20 V, respectively.
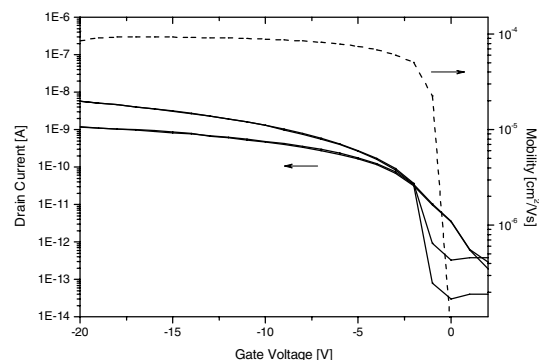
Figure 10. Transfer characteristics of **3**. The drain potentials were -20 V and -2 V in the upper and lower traces, respectively (solid lines). The dashed curve shows the mobility values.
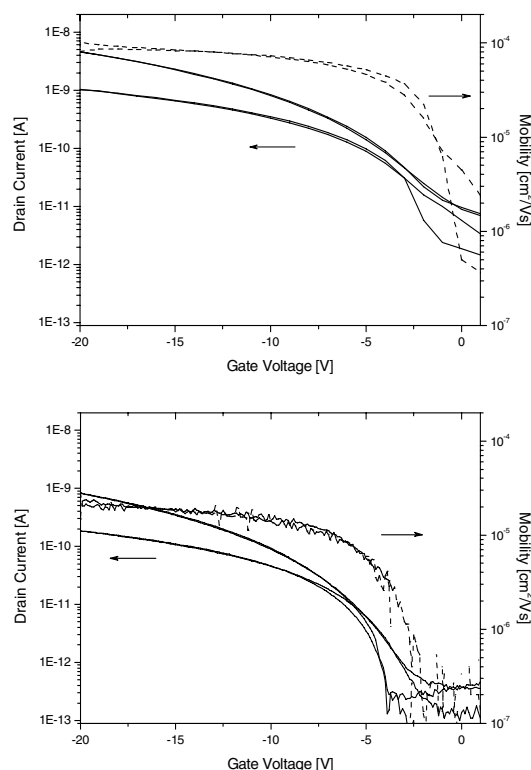
Figure 11. Transfer characteristics of **4**. The drain potentials were –20 V and - 2 V in the upper and lower traces, respectively (solid lines). The transistor shows only very small hysteresis in the forward/backward sweeps. The dashed curve shows that the mobility almost reaches its maximum directly after turning on the FET device. Above: freshly prepared device. Below: device performance after storage under ambient conditions and daylight for 4 months.

The mobility μ$_{FET}$ was calculated from the gate sweep according to the following equation

$$\mu_{FET} = \left(\frac{L}{W \cdot C \cdot V_D} \right) \frac{\partial I_{SD}}{\partial V_G}$$

where L is the channel length, W is the channel width, C the capacitance of the insulator per unit area, V_D is the drain voltage, I_D is the drain current and V_G is the gate voltage.

The transfer characteristics of an OFET from **3** are shown in Fig. 10. The molecular glass **3** exhibits a field-effect mobility of 10^{-4} cm^2/Vs, an on/off ratio of 10^4 and a very low turn on voltage of about -2 V. A very important property of organic materials to be used in OFETs is their stability under ambient conditions. The field-effect transistor from the star-shaped compound **4** was stored for 4 months in air and light in the laboratory and then tested again, with the result that both the onset voltage and the on/off ratio did not change. Only the field-effect mobility dropped to a value of 2 x 10^{-5} cm^{2}V^{-1}s^{-1}. The transistor characteristics of **4** before and after the storage period are presented in Fig. 11. The very good long term stability under ambient conditions is probably the most promising result of our transistor measurements.

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Author Biography

Peter Strohriegl received his PhD in macromolecular chemistry from the University of Marburg in 1984. Since then he has worked at the University of Bayreuth. His work has focused on the development of new photoconductors and of materials for organic light emitting diodes and polymer electronics.