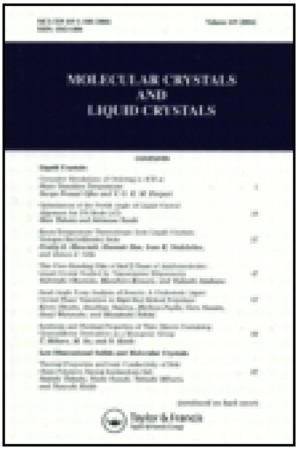

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Carbazol-3-yl Substituted Aromatic Amines Containing Crosslinkable Groups as Materials for Multilayer Light Emitting Diodes

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Carbazol-3-yl Substituted Aromatic Amines Containing Crosslinkable Groups as Materials for Multilayer Light Emitting Diodes

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A series of cross-linkable aromatic amines which are potential materials for hole-transporting layers have been examined by various techniques including differential scanning calorimetry, thermogravimetry, and electron photoemission spectrometry. Hole transport properties of the materials were tested in two-layer light emitting diodes with Alq_3 as the electroluminescent and electron transporting material. One derivative was applied for the preparation of insoluble electro-active layers by cationic photo-initiated polymerization. Atomic force microscopy was used for the investigation of photopolymerized films which were tested as insoluble hole transporting layers in a device with Alq_3.

Keywords: aromatic amine; crosslinkable material; ionization potential; light emitting diode

1. INTRODUCTION

Efficient organic light-emitting diodes (OLEDs) can be obtained by building multilayer structures [1]. Two approaches can be used for their fabrication. The organic layers can be fabricated by vapour deposition or by spin coating from a solution. The latter rout has some advantages, e.g., the production costs are reduced, large areas can

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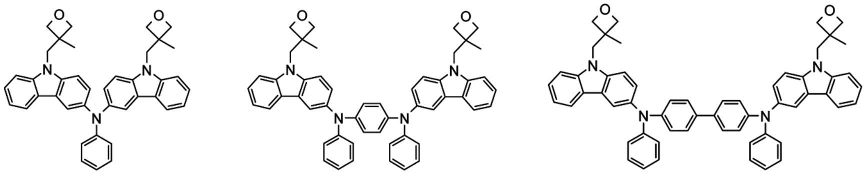
be coated, and the molar mass of materials is not limited. A severe difficulty in the preparation of such devices is the solubility of a material which forms the bottom layer, onto which the top layer has to be cast, because most organic semiconductors are soluble in the same organic solvents. One approach that has been employed to circumvent this problem is to render the material insoluble by using cross-linking reactions.

Recently, several series of photocrosslinkable polymers [2] and monomers [3] for the fabrication of OLEDs have been reported. Among the photocrosslinkable monomers earlier studied, triphenyldiamine (TPD) core having derivatives were mostly used. Here, we present new crosslinkable derivatives containing carbazolyl fragments. Films of the compounds demonstrate the suitable hole injection and transport properties as demonstrated in multilayer OLEDs. One of the derivatives was converted to an insoluble hole-transporting network and used in the preparation of the device with Alq_3 as the electroluminescent and electron transporting material.

2. EXPERIMENTAL

Materials used for the preparation of hole-transporting layers – N,N-di[9-(3-methyloxetan-3-ylmethyl)carbazol-3-yl]-N-phenylamine (**1**), N,N′-di [9-(3-methyloxetan-3-ylmethyl)carbazol-3-yl] - N,N′-diphenyl-1,4-benzenediamine (**2**) and N,N′-di[9-(3-methyloxetan-3-ylmethyl)carbazol-3-yl]-N,N′- diphenylbenzidine (**3**) are shown in Scheme 1. The derivatives were synthesized by procedures described earlier [4].

Differential scanning calorimetry (DSC) measurements were carried out using a Bruker Reflex II thermosystem. Thermogravimetric analysis (TGA) was performed on a Netzsch STA 409. The TGA and DSC curves were recorded in a nitrogen atmosphere at a heating rate of 10°C/min. Atomic force microscopy (AFM) characterizations of topographical images were done with an SPI3800N AFM



SCHEME 1 Materials used for the preparation of hole-transporting layers.

instrument (Seiko Instruments Inc., Japan) in the tapping mode with a $2\,\mathrm{Nm}^{-1}$ probe and a scan rate of 1.44 Hz under ambient conditions.

The ionization potentials of layers of the compounds synthesized were measured by the electron photoemission method in air which was described earlier [5]. The measurement method was, in principle, similar to that described by Miyamoto *et al.* [6]. The samples for the ionization potential measurement were prepared as described previously [7].

Thin films of the materials were prepared by spin-coating from their chloroform solutions (∼20 mg/ml). The films for photocross-linking were prepared from the solutions which additionally contained 2–5 wt% of {4-[(2-hydroxytetradecyl)-oxyl]-phenyl}-phenyliodonium hexafluorantimonate (**PhIA**) as a cationic photoinitiator. These films were irradiated with a standard handheld UV lamp for ca. 90 s at room temperature. Afterwards, to further advance the crosslinking process in the growing network, the films were annealed at 125°C for 3 min. Then the films were rinsed with THF and finally heated to 180°C for 5 min.

The multilayer electroluminescent devices were fabricated on glass substrates and had the typical structure with the organic layers sandwiched between a bottom ITO anode and a top metal cathode. The hole-transporting layers were prepared by the spin-coating of a 30–40-nm layer of derivatives **1–3**. The films of material **3** containing initiator **PhIA** were used for the preparation of insoluble electroactive layers by using the photocross-linking procedure as described above. Evaporation of the electroluminescent tris(quinolin-8-olato)aluminum (Alq_3) layer (70 nm) and a LiF/Al electrode (1/150 nm) was done at a pressure of $3 \cdot 10^{-6}$ mbar in a vacuum evaporation equipment. The current-voltage and luminance-voltage characteristics were recorded under the forward bias using a computer-controlled Keithley 2400 source meter and a PR650 Spectrometer. All the measurements were performed under ambient conditions in air.

3. RESULTS AND DISCUSSION

The thermal properties of compounds (**1–3)** were studied by DSC and TGA in a nitrogen atmosphere. It was observed that all the aromatic amines demonstrate high thermal stability. Their temperatures of the initial destruction range from 383 to 397°C as confirmed by TGA.

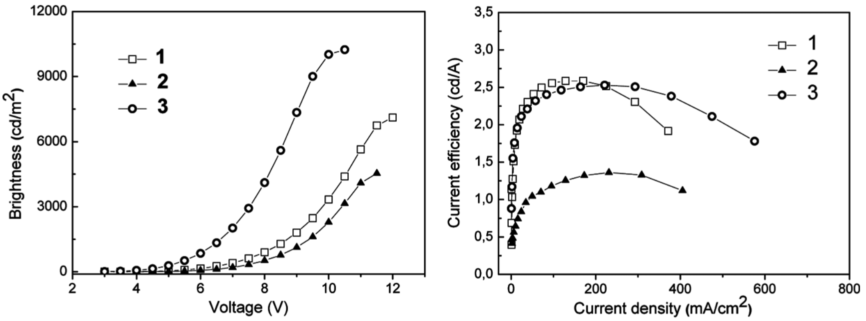
Derivative **1** was obtained in nature as an amorphous material. When its sample was heated during DSC, the glass transition temperature (T_g) was observed at 120°C, and no peaks due to crystallization and melting appeared. Derivatives **2** and **3** were obtained as crystalline materials after syntheses; however, they readily formed glasses when their melt samples were cooled on standing in air or with liquid nitrogen. The values of T_g were 126°C for **2** and 144°C for **3**.

The electron photoemission technique was used to estimate the ionization potentials (I_p) of thin amorphous films of compounds (**1–3**). The layer of compound **1** has the lowest I_p equal to 5.1 eV. The ionization potentials of thin layers of materials **2** and **3** are rather close (ca. 5.25 eV). It should be mentioned that the values of I_p of the layers prepared with the use of (**1–3**) are lower than those of widely used low-molecular-weight hole-transporting materials TPD [8] and 1,4-bis(1-naphthylphenylamino)biphenyl (NPD) [9]. On the other hand, I_p of compounds **1–3** are very close to that of ITO ($\sim$4.9 eV) which is usually used as an anode in electroluminescent devices [10]. The injection barrier of holes from the electrode into the layers of materials **1–3** would be only 0.2–0.3 eV. These findings demonstrate that carbazol-9-yl substituted aromatic amines are promising materials for hole-transporting layers in multilayer OLEDs.

Materials **1–3** were tested in two-layer OLEDs. Compounds **1**, **2**, or **3** were used as the hole-transporting (HT) layers and Alq_3 as an electroluminescent and electron-transporting layer. The cathode used was aluminum with a thin LiF electron injection layer. When a positive voltage was applied, the bright green electroluminescence of Alq_3 was observed from all the devices with an emission maxima at around 520 nm [11,12]. This implies that the hole mobility in the HT layers of **1–3** is fully sufficient for the effective charge carrier recombination occurring within the Alq_3 layer.

Figure 1 shows the luminance – voltage characteristics and efficiencies for the OLEDs containing the HT layers of (**1–3**). These devices exhibit, in general, turn-on voltages of 4–5 V, a photometric efficiency of 1.4–2.6 cd/A, and a maximum brightness of 4500–10200 cd/m^2 (at 10–12 V). Among these OLEDs, the device with derivative **3** as the HT material exhibits the highest brightness. However, the device with **1** demonstrates the best overall performance with an efficiency of 2.6 cd/A.

Compound **1**, which was the most effective HT material in analogous devices, was investigated as a cross-linkable material for the preparation of insoluble electroactive layers. The photoinitiated cross-linking of its layers containing 2 or 5 wt% of cationic photoinitiator **PhIA** was performed as described in Section "Experimental." The solubility of the cross-linked layers was studied afterwards by measuring their UV spectra before and after the washing with THF which is an excellent solvent for non-cross-linked materials. Figure 2 shows the results for the films of **1** which were crosslinked by using different



(a) (b)

FIGURE 1 OLED characteristics of the devices with the configuration: ITO/material **1**, **2** or **3** /Alq$_3$/LiF/Al; (a) luminance – voltage and (b) efficiency – current density plots.

amounts of photoinitiator **PhIA**. If the cross-linking was performed with 2 wt% of the photoinitiator, the films remained almost soluble. This is clearly visible from the reduced absorption after the THF treatment. In contrast, the cross-linking with 5 wt% of the photoinitiator yielded insoluble films as documented by practically unchanged absorption spectra. These experiments demonstrate that the relatively

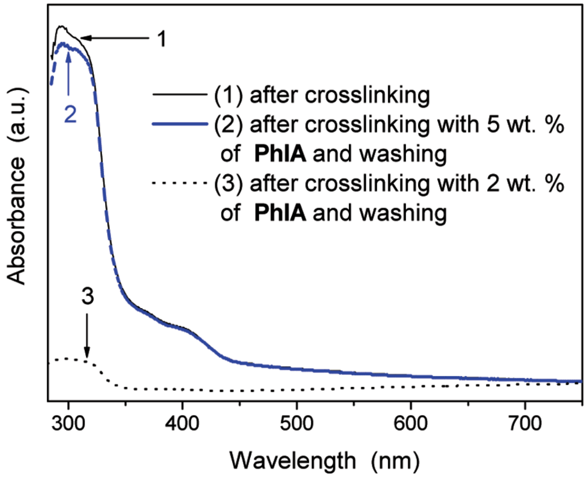


FIGURE 2 Absorption spectra of **1** films cross-linked on ITO with different amounts of the photoinitiator **PhIA**.

large amount of the photoinitiator is required for the preparation of insoluble films.

The nature of cross-linked films of **1** was studied using atomic force microscopy (AFM). The AFM profiles and the cross sectional roughness profiles of the cross-linked polymer film and those of the polymer film after the washing with THF, as well as after the post-curing, are given in Figure 3. For the comparison, the profiles of the ITO film are also presented. It can be clearly seen that the ITO film is crystalline with a very rough surface showing the peaks due to the crystals. After

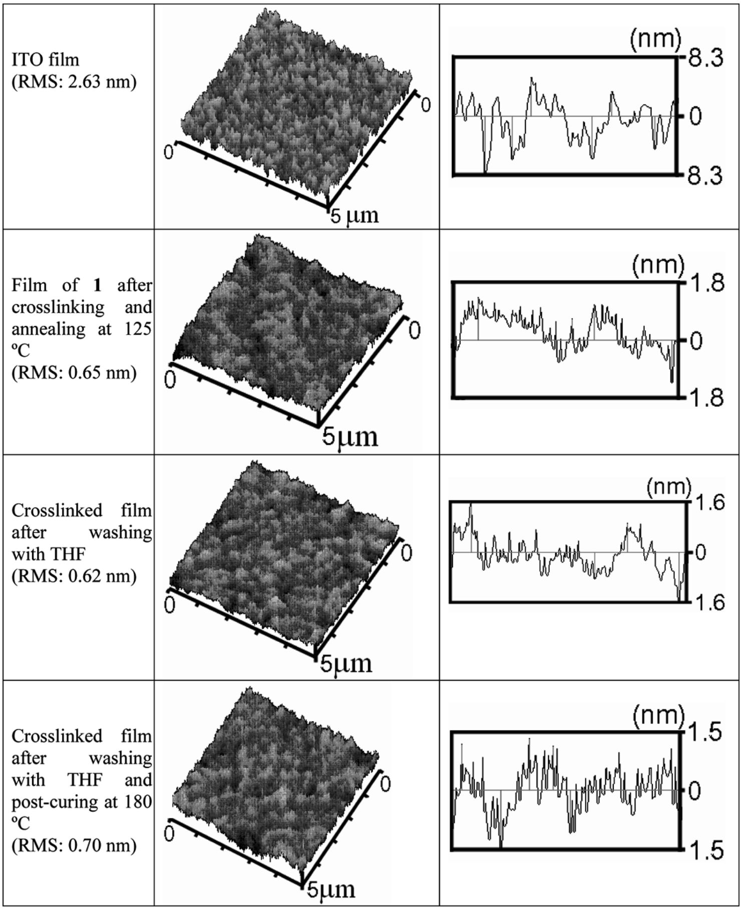


FIGURE 3 AFM profiles and cross-sectional roughness of ITO film and of material **1** film after cross-linking, after washing the cross-linked polymer film with THF and after post-curing.

the layer of **1** was spin-coated onto the ITO layer and cross-linked, it became almost smooth. The AFM root mean square (RMS) roughness was 0.65 nm. After washing the film with THF, it did not dissolve, and the RMS remained almost unchanged (0.62 nm). The following post-curing did not change the profile and the roughness of the film. These pictures demonstrate the advantage of cross linking in obtaining the insoluble and smooth polymer films for suitable applications in optoelectronics.

The cross-linked layers of compound **1** were tested as HT networks in two-layer OLEDs of the configuration ITO/ crosslinked **1**/ Alq_3(70 nm)/ (LiF/Al). The hole-transporting layers were made by the spin-coating of a 30–40-nm layer of derivative **1** containing initiator (5 wt%) from a solution onto the substrates with ITO and by the following cross-linking as described in Section “Experimental.”

The electroluminescence (EL) spectrum of the device containing an insoluble HT layer of cross-linked material **1** is shown in Figure 4. The EL spectrum of an analogous device with the uncross-linked layer of **1** is shown for the comparison. When a positive voltage was applied to the device, the bright green electroluminescence of Alq_3 was observed with an emission maximum at around 520 nm. This confirms that the insoluble network of **1** operates well as a hole-transporting layer and its positive charges mobility is sufficient for the charge carrier recombination occurring within the Alq_3 layer. The comparison of

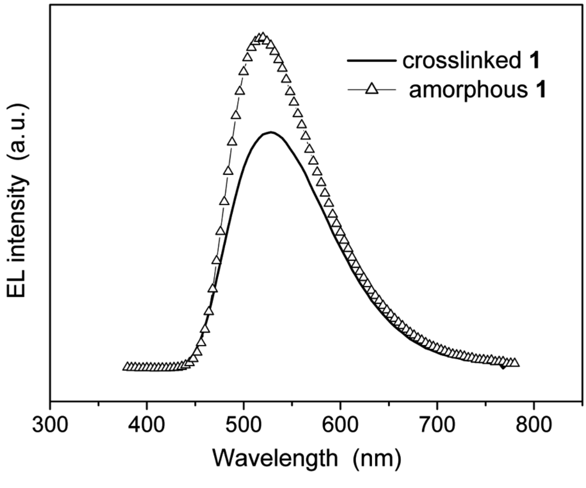


FIGURE 4 Electroluminescence spectra of the devices ITO/ material **1**/ Alq_3/ (LiF/Al).

EL spectra of the devices containing cross-linked and uncross-linked layers of **1** demonstrates that the photocross-linking has no influence on the emission spectrum of OLEDs. No exciplex formation at the interface between the hole transporting network and the Alq_3 layer is observed.

Figure 5 shows the current density-voltage-luminance characteristics of the device containing HT network of **1**. The current density increases exponentially with increase in the forward bias voltage, which is a typical diode characteristic. The rather low turn-on voltage of 5 V defined as the voltage, where electroluminescence (EL) becomes detectable, and the relatively low operation voltage ($100\,cd/m^2$ at $\sim$8 V) of this device suggest that the cross-linked layer of **1** can function well as an HT layer. As shown in the inset in Fig. 5, the maximum EL efficiency of the device exceeds 0.8 cd/A. It should be pointed out that these characteristics were obtained in a non-optimized test devices under ordinary laboratory conditions. The device performance may be further improved by the optimization of layer thicknesses and processing conditions.

In conclusion, cross-linkable monomers with the carbazolyl-substituted arylamine core as a hole-transporting moiety and reactive oxetanyl groups have been synthesized and characterized. All the materials are thermally stable and form amorphous films with glass transition temperatures in the interval of 120–144°C.

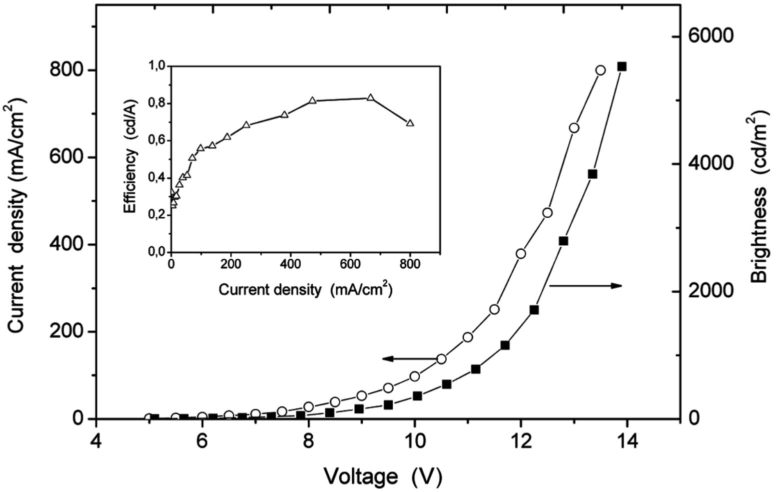


FIGURE 5 OLED characteristics of the device ITO/crosslinked **1**/Alq_3/(LiF/Al).

Insoluble and smooth films have been obtained from one of the derivatives by photoinduced cationic cross-linking. The cross-linked networks have been tested as hole-transporting layers in bilayer OLEDs with Alq_3 as an emitter and an electron-transporting material.

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