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Hole Transport Polymers with Improved Interfacial Contact to the Anode Material

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New hole transport polymers have been prepared through copolymerization of a fluorinated triphenyl diamine derivative and trimethoxyvinylsilane. The modification with trimethoxysilane groups has resulted in materials which can be cross-linked through hydrolysis and are capable of forming covalent chemical bonds to oxidic surfaces. Organic light-emitting diodes containing these polymers show decreased operating voltages and enhanced operational stability due to improved interfacial contact between the hole transport layer and the anode.

Introduction

The performance of organic light-emitting diodes (OLEDs) has greatly improved in recent years and is now approaching commercially viable levels. In particular, multilayer devices consisting of a thermally deposited hole transport layer (HTL) and emission layer have shown promising properties such as high brightness and efficiency, low operating voltage, and good operational stability.[1]

Additional improvements can be achieved by using hole-transporting polymers instead of the thermally deposited small-molecule materials to prepare the HTL. Polymer films can be prepared by spin-casting from solution, which is a more cost-effective method for the fabrication of the hole transport layer. High glass transition temperatures and the possibility to cross-link[2,3] the polymer can potentially increase the thermal and operational stability of the device. Furthermore, excellent film formation properties of the polymeric materials result in improved device performance compared to those of OLEDs containing the analogous small-molecule HTL.[4,5]

In our previous work we investigated polymeric triphenyl diamines (TPD) derivatives as hole-transporting materials in organic two-layer LEDs.[5,6] OLEDs with poly-TPD as HTL exhibited operating voltages 8 V lower than the analogous small-molecule-TPD devices.[5] The quantum efficiencies increased with increasing ionization potential (IP) of the HTL material.[7] The optimization of the device structure resulted in the fabrication of an OLED with 20 L·m/W efficiency using the fluorinated derivative **1** (Figure 1).[5] However, operational stability also depended on the IP. The device lifetime decreased as the IP of the HTL increased.[6,8] Consequently, the most efficient device was less stable than OLEDs with low-IP hole transport materials.

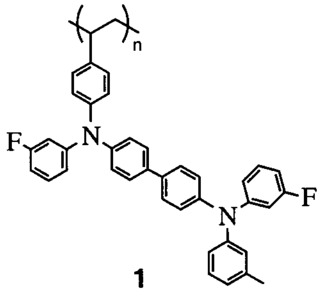

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Figure 1. Structure of the fluorinated triphenyl diamine (FTPD) derivative polymer.

Careful examination of the time−voltage curves obtained in constant-current lifetime experiments led us to believe that one of the major decomposition mechanisms is possibly due to poor adhesion of the HTL to the anode. Even though the initial interfacial contact is good, exposure to current and, consequently, heat

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[8] A similar trend has been shown for small-molecule HTL: Adachi, C.; Nagai, K.; Tamoto, M *Appl. Phys. Lett.* **1995**, *66*, 2679.

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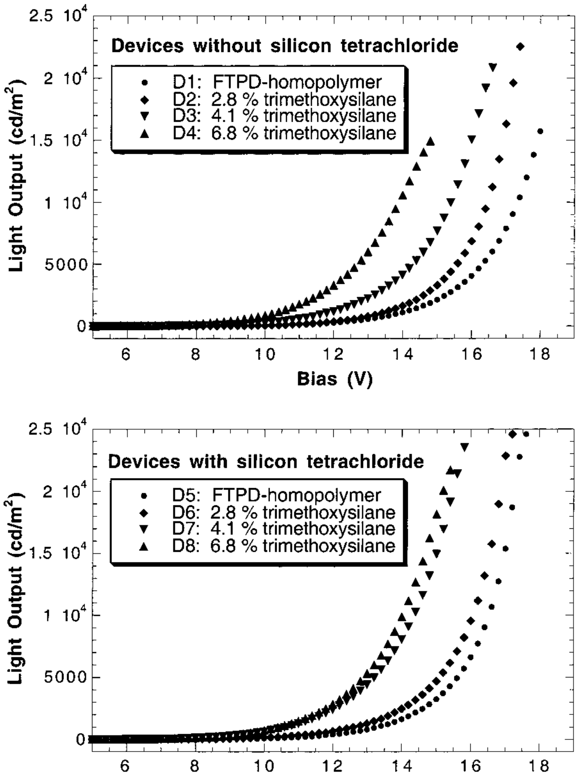


Figure 2. Light output versus voltage for the devices **D1**–**D8**.

resulted in partial delamination of the device causing a respective increase in contact resistance. The increased resistance was observed in our experiments through a substantial increase in voltage immediately after the beginning of current flow (Figure 3, curve D1).

Herein, we report the incorporation of trimethoxyvinylsilane into polymer **1** and the use of these modified HT polymers in OLEDs. Upon hydrolysis trimethoxysilanes cross-link and form covalent bonds with oxidic surfaces (Scheme 1).[9] Therefore, the connection between the silanated HTL and the indium–tin oxide (ITO) anode is based on chemical bonding and not physical adsorption, which in turn results in stronger adhesion of the HTL to the ITO. A procedure to cross-link the hole transport polymer to a glass surface is described. Improved adhesion behavior of silanated HTL under operating conditions of an OLED is demonstrated, and the dependence of device performance on the trimethoxysilane content of the HTL was investigated.

Experimental Section

General. All syntheses were carried out under argon, which was purified by passage through columns of BASF R-11 catalyst (Chemalog) and 4-Å molecular sieves (Linde). NMR spectra were recorded on a JEOL GX-400 spectrometer (399.65 MHz for ^{1}H). Gel permeation chromatograms were obtained on a HPLC system using an Altex model 110A pump, a Rheodyne model 7125 injector with a 100-mL injection loop, American Polymer Standards 10-μm mixed-bed columns, a Knauer differential refractometer, and CH_2Cl_2 as the eluent at a 1.0 mL/min flow rate. Differential scanning calorimetry was carried out on a Perkin-Elmer DSC-7 with a scan rate of 10 °C/min.

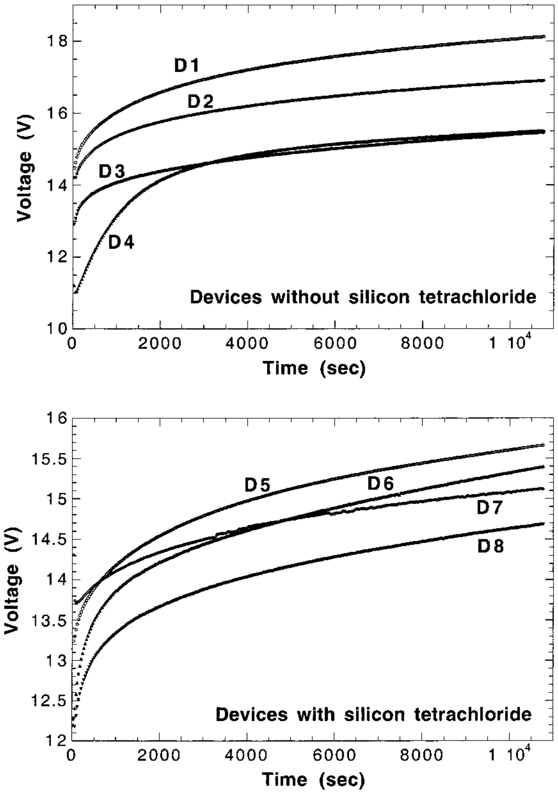
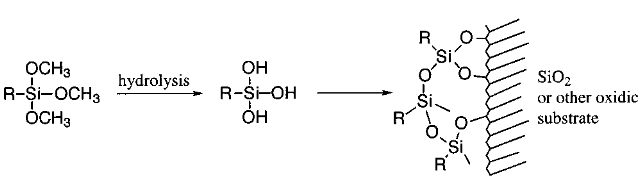


Figure 3. Voltage–time curves for the devices **D1**–**D8** (at 50 mA/cm^2).

Scheme 1: Reaction of Trimethoxysilanes with Oxidic Surfaces



Materials. Toluene and tetrahydrofuran (THF) were distilled from Na/benzophenone. Deuterated methylene chloride was dried by reflux over calcium hydride and vacuum-transfered into a flame-dried Schlenk flask. Monomer **2** was synthesized as previously reported.[6] Trimethoxyvinylsilane was obtained from Gelest, Inc. All other chemicals were obtained from Aldrich Chemical Co. and were used without further purification.

Preparation of Polymer 1 by Radical Polymerization. A solution of monomer **2** (1 g) and 2,2′-azobisisobutyronitrile (AIBN) (20 mg) in toluene (2 mL) was heated to 80 °C for 30 h. The polymer was purified by precipitation into methanol. Yield: 80%. PDI = 1.53. $M_w = 13\,000$ (determined by GPC in methylene chloride relative to polystyrene standards). ^{1}H NMR (CD_2Cl_2), all peaks are broad: δ 7.5, 7.2, 6.9, 6.5, 2.3, 2.2, 1.6.

Copolymerization Procedure. An excess of the comonomer trimethoxyvinylsilane (TVS) was added to the solution of monomer **2** (1 g) and 2,2′-azobisisobutyronitrile (AIBN) (20 mg) in toluene (2 mL), and the mixture was heated to 80 °C for 30 h. The polymer was purified by precipitation into dry methanol under argon, redissolution in dry THF, and reprecipitation into dry methanol. The reprecipitation was undertaken five times to ensure removal of excess comonomer. Subsequently, the solvents were removed in vacuo, and the copolymer samples were stored under argon excluding air moisture. The samples were checked for the absence of monomeric TVS by NMR. Different amounts of trimethoxyvinylsilane (TVS) in the feed resulted in different contents of trimethoxysilane in the copolymer. The trimethoxysilane content in the polymer samples was determined by taking ^{1}H NMR with 64 scans and

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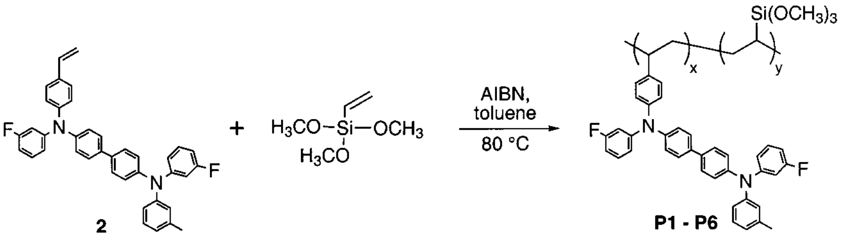
[9] Ulman, A. *Adv. Mater.* **1990**, *2*, 573, and references therein.

Scheme 2: Preparation of the Copolymers



10-s delay time and integration of the aromatic region versus the trimethoxysilane peak. ^{1}H NMR (CD_2Cl_2), all peaks are broad: δ 7.5, 7.2, 6.9, 6.5 (24 H, aromatic region), 3.3 (9 H, trimethoxysilane), 2.3, 2.2, 1.6, 0.9. A determination of the PDI and the molecular weight of the copolymers was not undertaken because the partially reactive polymer could be incompatible with the GPC columns.

Cross-linking of the Copolymers on Glass. Glass slides (Corning) were heated to 80 °C for 30 min in a mixture of 1 part 30% aqueous hydrogen peroxide solution and 3 parts concentrated sulfuric acid. After the slides were rinsed with copious amounts of deionized water, they were sonicated in a mixture of 5 parts water, 1 part ammonium hydroxide, and 1 part 30% aqueous hydrogen peroxide solution for 30 min. The slides were again washed carefully with deionized water and placed in an oven to dry for 5 min at 120 °C. Solutions of the copolymers in dry THF were prepared at a concentration of 10 mg/mL, and silicon tetrachloride (20 μL/mL) was added immediately prior to the preparation of the films. The films were heated to 120 °C for 14 h.

Fabrication of Light-Emitting Devices. Devices were fabricated on ITO-coated glass substrates (Donnelly Corp.) with a nominal sheet resistance of 40 Ω/sq which had been ultrasonicated in acetone, methanol, and 2-propanol, dried in a stream of nitrogen, and then plasma-etched for 60 s. Polymer layers (40 nm) were formed by spin-casting from solutions in dry THF (10 g/L). For the fabrication of devices with cross-linked HTL silicon tetrachloride (20 μL/mL) was added to the polymer solutions before spin-casting. The HTL films were heated to 120 °C in moist air. The second layer consisted of vacuum vapor-deposited tris(8-quinolinato)aluminum (Alq) (60 nm), which had been purified by recrystallization and sublimation prior to deposition. Subsequently, a layer of CsF (7−8 Å) was evaporated, and the aluminum cathode (150 nm) was thermally deposited through a shadow mask, creating devices of 0.1 cm^2 in active area. Cathode deposition and device characterization were performed in a nitrogen drybox (Vacuum Atmospheres).

Characterization of Light-Emitting Devices. Current−voltage and light output characteristics of the devices were measured in forward bias. Device emission was measured using a silicon photodetector at a fixed distance from the sample (12 cm). The response of the detector had been calibrated using several test devices, for which the total power emitted in the forward direction was measured with a NIST traceable integrating sphere (Labsphere). Efficiencies were measured in units of external quantum efficiency (% photons/electron). The lifetime experiments were done using a constant-current mode of 5 mA resulting in a current density of 50 mA/cm^2.

Results and Discussion

Copolymer Synthesis. Polymer **1** has originally been prepared through anionic polymerization of monomer **2** (Scheme 2).[6] A copolymerization of **2** with monomers containing the trimethoxysilane group by this method is not possible because anionic initiators decompose in the presence of trimethoxysilanes. Therefore, the polymerization of **2** was undertaken under radical conditions yielding polymer **1** with PDI = 1.53 and T_g = 141 °C.

Table 1. Preparation and Composition of the Trimethoxysilane-Containing Hole-Transporting Copolymers

copolymer	equivalents of TVS in the feed	% trimethoxysilane in the copolymer[a]
P1	2	0.9
P2	5	1.6
P3	8	2.8
P4	10	4.1
P5	13	6.0
P6	16	6.8

[a] The composition was determined by integration of the ^{1}H NMR spectra. The percentage was calculated as % by mass, taking into account the different molecular weights of monomer **2** and TVS.

TVS was chosen as the comonomer because of its simple compact structure and commercial availability. The reactivity of TVS under radical conditions is low. The reactivity ratios for the copolymerization of styrene and TVS are 20 and 0,[10] showing that under these circumstances TVS never reacts with itself. These data suggest that a block copolymer would not be formed and incorporation of TVS into the backbone of the polystyrene-type polymer **1** would proceed at random and in small amounts. Such behavior is advantageous for the application because only small amounts of TVS should be present within the hole transport material and a blocky structure containing polyTVS segments is undesirable.

Copolymers **P1**−**P6** with varying contents of trimethoxysilane were prepared by radical polymerization using a large excess of TVS (Scheme 2, Table 1). Trimethoxysilane contents from 0.9−6.8 wt % were achieved. The lowest content of trimethoxysilane corresponds to an FTPD/$Si(OCH_3)_3$ ratio of 28 or in other words to 3.4 mol % trimethoxysilane. A trimethoxysilane content of 6.8 wt % is equivalent to an FTPD/$Si(OCH_3)_3$ ratio of 3.6 or to 21.7 mol % of trimethoxysilane.

Cross-Linking of the Copolymers to Glass. Procedures for the reaction of trimethoxysilanes with cleaned and activated glass surfaces have previously been described.[9] To test the reactivity of the copolymers **P1**−**P6**, films of the polymers were spin-cast on glass slides which were pretreated with piranha solution and a mixture of ammonium hydroxide and hydrogen peroxide. Films prepared from polymer solutions in dry THF remained soluble after being heated in moist air to 120 °C overnight. Addition of small amounts of water or HCl to help the hydrolysis of the trimethoxysilane group resulted in opaque films that would not be suitable for application in OLEDs. Successful cross-linking was achieved through addition of tetrachlorosilane (20 μL for 1 mL of polymer solution in dry THF)

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(10) Brandrup, J., Immergut, E. H., Eds. *Polymer Handbook*; John Wiley & Sons: New York, 1975.

Table 2. Composition of the HTL and Performance of the ITO/HTL/Alq/CsF/Al Devices

device	HTL	ext. quant. eff. (% photons/e$^-$)[a]	operating voltage[b] (V)	increase in voltage[c] (%)[d]
D1	**1**	1.3	8.6	28
D2	**P3**	1.4	8.2	18
D3	**P4**	1.4	6.8	19
D4	**P6**	1.2	5.8	38
D5	**1** + $SiCl_4$	1.3	7.2	18
D6	**P3** + $SiCl_4$	1.5	7.4	10
D7	**P4** + $SiCl_4$	1.5	6.2	19
D8	**P6** + $SiCl_4$	1.5	6.0	26

[a] Peak external quantum efficiency as determined from the current−voltage behavior. [b] Light output at this voltage equals 5 cd/m^2. [c] After 3 h of continuous operation at 50 mA/cm^2. [d] % of initial voltage at the beginning of the lifetime experiment.

and subsequent heating of the films to 120 °C for 14 h. The resulting films were transparent, exhibited blue-violet fluorescence, and did not redissolve in THF or methylene chloride. This procedure was used to prepare hole transport layers on ITO during the fabrication of light-emitting diodes.

Fabrication and Characterization of OLEDs. Organic light-emitting diodes of the configuration ITO/HTL/Alq/CsF/Al were fabricated (ITO = indium tin oxide, Alq = tris(8-quinolinato)aluminum). The hole transport layers were prepared through spin-casting of one of the copolymers **P3**, **P4**, and **P6** out of solutions in dry THF to which tetrachlorosilane was added. In control experiments copolymer-HTLs were prepared without $SiCl_4$, and polymer **1** was used as hole transport material with and without the additive. In all cases, the hole transport layers on ITO were heated to 120 °C for 14 h prior to thermal deposition of the emissive layer and the cathode. Table 2 shows the compositions of the hole transport layers and the performance parameters of the corresponding devices.

An examination of the initial performance of the OLEDs revealed that the maximum external quantum efficiency was not affected by addition of $SiCl_4$ or incorporation of trimethoxysilane units into the hole-transporting polymer. In contrast to a previous study in which devices with a cross-linked hole transport layer showed decreased performance compared to LEDs containing the soluble parent polymer,[3] addition of the cross-linking reagent $SiCl_4$ to the HTL polymers did not alter the external quantum efficiency of the device. The external quantum efficiency was also independent of the trimethoxysilane content of the copolymers. All of the devices **D1**−**D8** showed the same external quantum efficiency within the experimental error of ±0.1% photons/e$^-$. In conclusion, the trimethoxysilane method is a way to modify and cross-link the HTL without reducing the external quantum efficiency of the LED.

The operating voltage decreased significantly with increasing trimethoxysilane content of the HTL and was lowered further if the complete cross-link procedure with addition of $SiCl_4$ is performed (Table 2, Figure 2). This is indicative of the improved interfacial contact between the hole transport layer and the anode. The presence of Si−O moieties could not have enhanced the intrinsic charge injection and charge transport properties of the HTL because silicon oxides are insulators. Therefore, the overall reduction in operating voltage is to be attributed to better wetting and better surface coverage which results in a decrease of contact resistance at the ITO/HTL interface.

Interestingly, addition of silicon tetrachloride to polymer **1** also lowered the device operating voltage, even though **1** has no functional groups to react with $SiCl_4$. The hydrolyzed silicon tetrachloride apparently acts as an adhesion promoter in this case.

To characterize the operational stability of the devices **D1**−**D8**, the LEDs have been operated under constant-current conditions at 50 mA/cm^2. Figure 3 shows the obtained voltage−time curves. A fast increase in voltage indicates a substantial increase in contact resistance presumably due to delamination. The increase in voltage over a period of 3 h is reported in Table 2 in percentage of initial voltage. Addition of $SiCl_4$ resulted in a slower voltage increase in all cases. The hydrolyzed silicon tetrachloride clearly acted as an adhesion promoter because it also improved the voltage−time behavior of the parent polymer **1** which does not contain functional groups to react with the surface.

The increase in voltage also depended on the trimethoxysilane content of the copolymers. Copolymers with low trimethoxysilane contents performed better than the parent polymer. In particularly, device **D7** showed a relatively flatter voltage−time curve. Over the period of 3 h, and under such high current density, the voltage increased by only 10%, suggesting that the contact between the layers is good and device delamination is slow.

However, if the trimethoxysilane content is increased above 6%, it is no longer beneficial in terms of operational stability. Devices **D4** and **D8** showed a fast increase in voltage during operation at constant current. Even though the initial operating voltage for these devices was the lowest, the operational stability was less than that in the case of the parent device **D1**. The specific morphology at the ITO/HTL interface after hydrolysis of trimethoxysilane and $SiCl_4$ is not known. Further studies are needed to explain why there is a change in properties at a trimethoxysilane content of around 6%.

Summary and Conclusions

We have synthesized a series of copolymers containing a fluorinated TPD derivative as the hole-transporting functionality and small amounts of trimethoxysilane. These copolymers can be cross-linked onto an oxidic surface through addition of silicon tetrachloride and heating in moist air.

Two-layer LEDs containing these materials as the hole transport layer were fabricated. The peak quantum efficiency of the devices did not depend on the trimethoxysilane content or addition of the cross-linking reagent $SiCl_4$. The HTL can be prepared through spin-casting, and the subsequent cross-linking procedure did not decrease the device efficiency.

The initial operating voltage of the devices decreased with increasing trimethoxysilane content and was lowered further through addition of $SiCl_4$. The hydrolyzed trimethoxysilane improved the bond between the anode surface and the HTL, resulting in lower contact resistance and, consequently, lower operating voltage. Hydrolyzed silicon tetrachloride acted as an adhesion promoter because it also improved the properties of the FTPD homopolymer which does not have functional groups to chemically react with the ITO surface or $SiCl_4$.

The operational stability of the LEDs was studied in constant-current density experiments at 50 mA/cm^2. Copolymers with low contents of trimethoxysilane showed improved operational stability. The voltage increased slowly with time, indicating that the contact between the layers remains good. For a trimethoxysilane content above 6 wt %, the voltage increase was higher compared to the parent device, showing that, despite the low initial operating voltage, the operational stability was poor. To explain this change in properties, the specific morphology at the ITO/HTL interface after hydrolysis would need to be determined. Addition of silicon tetrachloride was beneficial in all cases and improved the operational stability of both the copolymer and the parent homopolymer devices.

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