Photo-Cross-Linked Triphenylenes as Novel Insoluble Hole Transport Materials in Organic LEDs

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ABSTRACT: A series of new hexaalkoxytriphenylenes having 1, 2, or even 3 lateral attached acrylate moieties as polymerizable groups were synthesized and characterized. The conditions for the photopolymerization of these monomers in thin film were evaluated and tested. The bisacrylates and trisacrylates were used to build insoluble networks. When a mask is used during the irradiation, patterned films could be prepared. The polymerization reaction was controlled by GPC and FTIR spectroscopy. The networks and patterned structure were confirmed by UV spectroscopy, surface profiles, and SEM photographs. Since hexaalkoxytriphenylenes are known as excellent photoconductors, the photopolymerized films were utilized as hole transport layers in two layered organic light-emitting diodes (LEDs) with Alq_3. The LED preparation, characterization, and performance are described.

Introduction

Electroluminescent devices based on organic low molecular weight[1,2] and polymeric[3,4] materials are recently attracting much attention mainly due to applications as large area light-emitting devices (LEDs).[5] Generally, these devices are thin-film single-layer or multilayer structures composed of a hole transport and an emitting and an electron transport material sandwiched between two electrodes. LED devices are generally fabricated utilizing vapor deposition techniques or film-casting techniques from solution.

A severe difficulty in the preparation of multilayered structures by solution film-casting techniques is the solubility of the bottom layer onto which the top layer film has to be casted. In principle, this problem can be avoided by using solvents of opposite polarity in which the bottom layer is not attacked by the casting solvent. The utilization of precursor polymers and a two-step preparation process as well established for poly(*p*-phenylenvinylene) (PPV) avoids this problem. A soluble PPV precursor is coated onto the ITO substrate and thermally converted into an insoluble PPV film.[6] In this process critical issues are the reproducibility of the film quality, optical and electrical properties,[7] and the fact that reactive volatile byproducts cause degradation of the ITO electrode.[8]

A chemically different approach to convert a soluble material into an insoluble material can be achieved by using photo-cross-linking reactions. This technique is well established in the coatings industry and in photoresist technology. The resulting cross-linked polymer layers are insoluble and not meltable.[9] Very recently, Bellmann et al. reported photo-cross-linkable triarylamine-containing polymers as novel hole transport materials in organic light-emitting diodes and their device characteristics.[10]

The class of hexaalkoxytriphenylenes is known for its excellent hole transport properties. Photoinduced charge carrier mobility ranges from 1×10^{-5} cm^2/(V s)[11] in the isotropic phase up to 1×10^{-2} cm^2/(V s)[12] in highly ordered discotic mesophases. These properties stimulated research toward an application in xerographic processes[13] and more recently as hole transport material in organic LEDs.[14,15] On the basis of two-layer LEDs with tris(8-quinolinolato)aluminum(III) complex (Alq_3) and soluble triphenylene derivatives, it was demonstrated that brightness and efficiency values can be achieved similar to devices built from typically used triphenyldiamine or triphenylamine derivatives.[15] However, triphenylene derivatives are readily soluble, thus allowing only the deposition of an emitting or electron transport material by vapor deposition techniques.

Therefore, this paper addresses the realization of triphenylene networks as an insoluble hole transport layer in light-emitting diodes. The photopolymerization conditions in thin layers were optimized with monofunctional monomers yielding to linear polymers. Photocross-linking of multifunctional triphenylene derivatives was confirmed by spectroscopic methods and by the preparation of a patterned structure. Additionally, the function of the cross-linked triphenylene layers in two-layer LEDs as hole transport layer was demonstrated.

Materials Synthesis

The materials used in this study possess 1, 2, or 3 polymerizable acrylate groups. The chemical structures of the monomers are summarized in Scheme 1.

The polymerizable acrylate groups are connected via alkoxy spacers to the triphenylene core. Butoxy side chains in **1** and **4** are combined with ethoxy spacers and pentoxy side chains in **2** and **3** with propoxy spacers. The synthesis follows new approaches combined with procedures described in the literature. The monoacrylate **1** was prepared by the so-called “biphenyl route” (Scheme 2) developed by Ringsdorf et al.[16] and Boden et al.[17] The etherfication of pyrocatechol with 1-bro-

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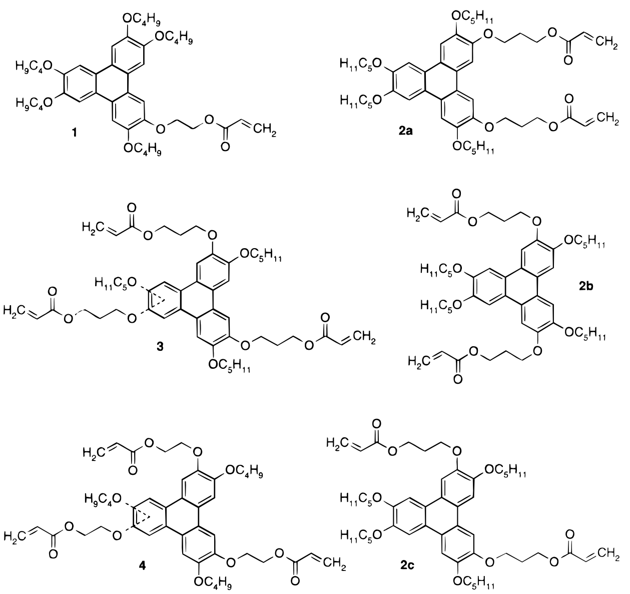
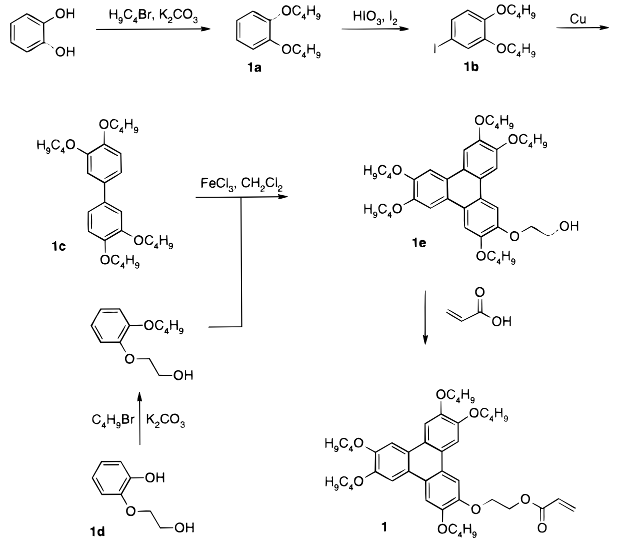


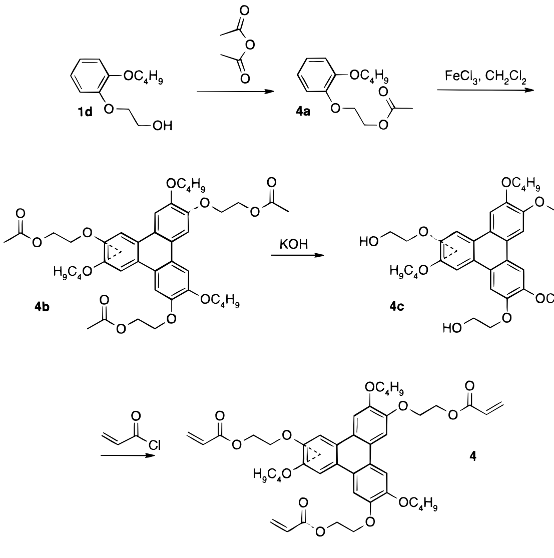
Scheme 1. Chemical Structure of the Mono-1, Bis-2a−c, and Trisacrylate 3,4 Derivatives of Hexaalkoxytriphenylenes



Scheme 2. Synthesis of 2-[(3,6,7,10,11-Pentabutoxy-2-triphenylenyl)oxy]ethyl Acrylate 1 via the "Biphenyl Route"

mobutane gives 1,2-dibutoxybenzene (**1a**). The iodination of **1a** with periodic acid[16,18] results in 3,4-dibutoxyiodobenzene (**1b**), and a subsequent Ullmann coupling[16,19] of **1b** leads to 3,3′,4,4′-tetrabutoxybiphenyl (**1c**). The reaction of 2-(2-hydroxyethoxy)phenol and 1-bromobutane yields 2-(2-butoxyphenoxy)-1-ethanol (**1d**). The biphenyl is subsequentely cyclized with iron(III) chloride and **1d** to obtain the 2-[(3,6,7,10,11-pentabutoxy-2-triphenylenyl)oxy]-1-ethanol (**1e**). In the final step, the aliphatic hydroxyl group of **1e** is reacted to the acrylate unit with acrylic acid to give the monomer 2-[(3,6,7,10,11-pentabutoxy-(2-triphenylenyl)-oxy]ethyl acrylate (**1**).

The bisacrylates **2a**−**c** are also prepared via the "biphenyl route". Starting from 2-pentoxyanisole followed by iodination with periodic acid and subsequent Ullmann coupling results in three isomeric biphenyls. Cyclization with 1,2-dipentoxybenzene yields three isomeric triphenylene derivatives with methoxy groups in the 2,6-, 3,6-, and 2,7-positions. Column chromatography provides the pure 3,6-isomer. Selective ether cleavage of the methoxy groups with diphenylphosphine anions leads to the dihydroxytriphenylenes.[20] In this step of the synthesis, the 2,6- and 2,7-isomers are separated by column chromatography. Introduction of the polymerizable groups is achieved with acryloyl chloride as described above.[20]



Scheme 3. Synthesis of the Trisacrylate Mixture 2,6,10-Tributoxy-3,7,11-tris(2-acryloxyethoxy)triphenylene and 2,6,11-Tributoxy-3,7,10-tris(2-acryloxyethoxy)-triphenylene 4

The trisacrylates **3** and **4** are synthesized following a different route (Scheme 3). Reacting 2-(2-hydroxyethoxy)phenol with 1-bromobutane or 1-bromopentane yields 2-(2-butoxyphenoxy)-1-ethanol (**1d**) or 3-(2-pentoxyphenoxy)-1-propanol, respectively. Cyclization of the acetyl-protected functionalized alcohols leads, after removal of the protecting groups, to the corresponding trifunctional triphenylenes. The lateral hydroxy groups of both resulting trihydroxy isomers are converted to the trisacrylates in a similar manner as described above. The isomers were not separated in these cases.

Photopolymerization of the Monofunctional Triphenylene 1

The monoacrylate **1** was used to evaluate and optimize the conditions for the photopolymerization in thin films and to verify the principal function of in situ polymerized HTLs in organic LEDs. All layers are prepared from a 1−1.5 wt % solution of the monomers in THF and 3 mol % Lucirin TPO (with respect to the triphenylene monomers) as photoinitiator. To optimize the processing and polymerization conditions as well as allowing spectroscopic characterization, a few drops of this solution were casted on a glass substrate, and the solvent was allowed to evaporate under ambient conditions to form a film of about 0.4−1 μm thickness. Polymeric films with the best optical quality are obtained by irradiating with a 150 W xenon lamp at 130 °C on a hot plate under a desiccator cover after evacuating and flushing with argon three times. The desiccator cover additionally serves as cutoff filter for higher energy UV light. In the region of the absorption of the photoinitiator the cover is transparent. The optical density of the cover is less than 1 for $\lambda > 320$ nm. The monoacrylate **1** exhibits a discotic hexagonal LC phase (k 66 D_h 121 i); experiments at lower temperatures

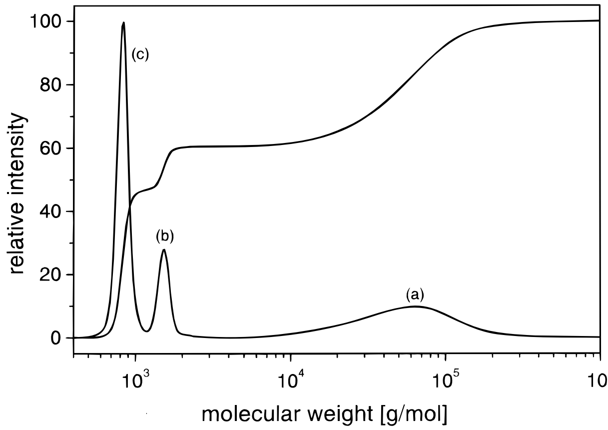


Figure 1. GPC chromatogram of an as polymerized film of **1** (eluent THF, standard PS).

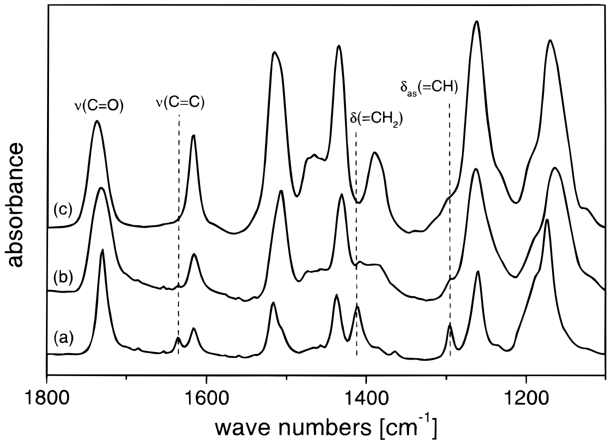


Figure 2. Spectroscopic verification of the photo-cross-linking reaction in thin films by FT-IR (16 scans; 4 cm^{-1} resolution, films on KBr): (a) trisacrylate **4** before polymerization, (b) photopolymerized film of **4**, and (c) reference spectrum of a polymer derived from solution polymerization of **1**.

within the LC phase were carried out but resulted in turbid films after polymerization, due to the domain structures of the LC phase. Therefore, all polymerizations were carried out above the clearing temperature. After polymerization the films consist of a mixture of polymer (a), remaining monomer (c), and some product with twice the molecular weight of the monomer (b). The exact composition of the mixture was determined by GPC (Figure 1) after dissolving the film from the glass substrate with benzene and subsequent freeze-drying. Typically, the rate of conversion during the polymerization is higher than 50%, and the yield of the polymer is about 40%. The polymeric fraction is characterized by $M_n = 38\ 600$ g/mol and $M_w = 68\ 700$ g/mol, resulting in a polydispersity $D = 1.78$.

Triphenylene Networks

To prepare polymeric networks, the bisacrylates **2** and trisacrylates **3** and **4** were used. Films polymerized under the same conditions as described above were spectroscopically investigated with FT-IR, using a KBr pellet as substrate. It is possible to verify a conversion of the acrylate moiety with transmission FT-IR spectroscopy. Typical vibration bands originating from the acrylate group can be seen in the case of the trisacrylates. Figure 2 shows the FT-IR spectra of a cast monomer film of **4** before photopolymerization (a) and of the cross-linked polymer network (b). For comparison,

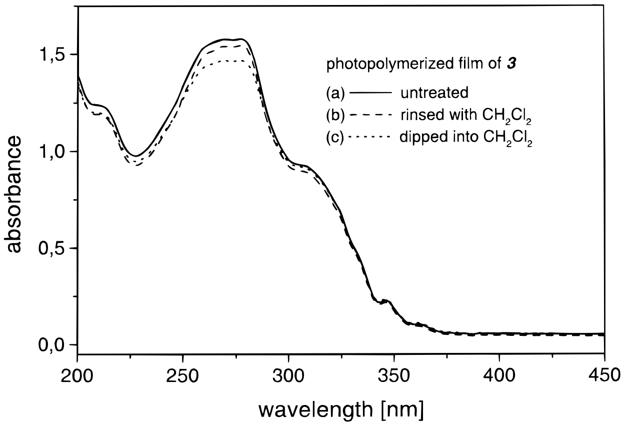


Figure 3. UV spectra of a cross-linked film of **3** on quartz: (a) untreated; (b) methylene chloride rinsed; (c) dipped in methylene chloride.

the spectrum of a solution polymerized polymer of **1** is included as (c). A very characteristic band is located at 1635 cm^{-1}, which can be attributed to the stretching vibration of the carbon−carbon double bond of the acrylic moiety that gives rise to another band due to structural isomerism at about 1620 cm^{-1}.[21] The latter one is not indicative since the stretching bands of the aromatic rings are overlapping. After polymerization the band at 1635 cm^{-1} has almost completely disappeared as well as several bands that can be attributed to different deformation vibrations of the C=C−H unit. The out-of-plane vibration band is located at 1411 cm^{-1} whereas the in-plane vibrations give rise to bands at 1280, 985, and 863 cm^{-1} [21] (latter two are not shown). These bands are also drastically reduced in intensity after photopolymerization. In comparison to the monoacrylate **1** the rate of conversion seems to be higher in the case of **4**, as estimated from the FT-IR spectra. This is likely since the density of acrylate moieties is much higher in the trisacrylate.

Polymerized films on quartz substrates were used to demonstrate the insolubility of the polymer network. In Figure 3 the UV absorption spectra directly after polymerization and after rinsing the film with methylene chloride or dipping into methylene chloride for several minutes show only a very slight decrease in absorbance. This demonstrates that almost all monomers are covalently incorporated into the network. The washing conditions applied were as rigorous as possible without mechanically washing the cross-linked film off the substrate. It should be noted that both the monomers and the linear polymer from triphenylene **1** are readily removed from the substrate by rinsing them once with methylene chloride or even less good solvents such as THF or benzene. No significant differences could be observed in experiments with the difunctional monomers **2a**−**c** and the trisacrylate **3**. All three bisacrylates and both trisacrylates yield insoluble polymer films after photopolymerization.

Photopatterning

These results make it also possible to photopattern the hole transport layer. The experiments described below were done with the trisacrylate monomer **4**. A photomask consisting of alternating 2 mm wide strips and 2 mm wide openings was used. To minimize backscattering of UV light from the hot plate, a blackened piece of metal is placed between the hot plate and

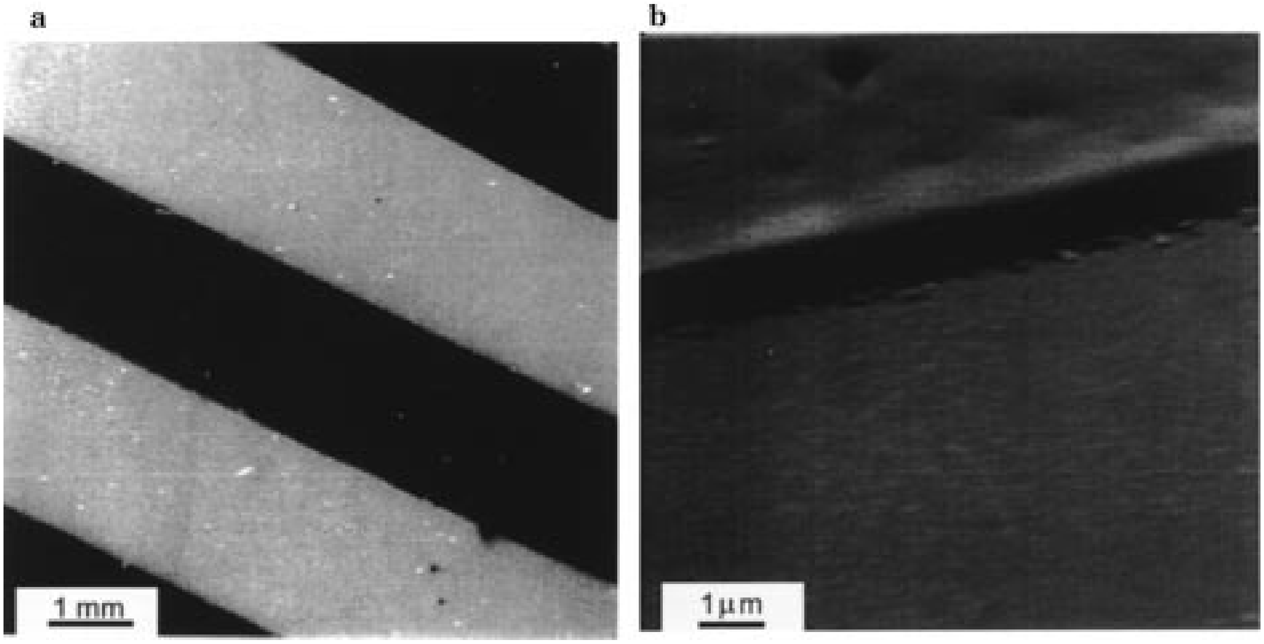


Figure 4. Scanning electron microscope photographs of a photopatterned structure of a polymer network from trisacrylate **3**: (a) top view in low resolution; (b) side view in high resolution.

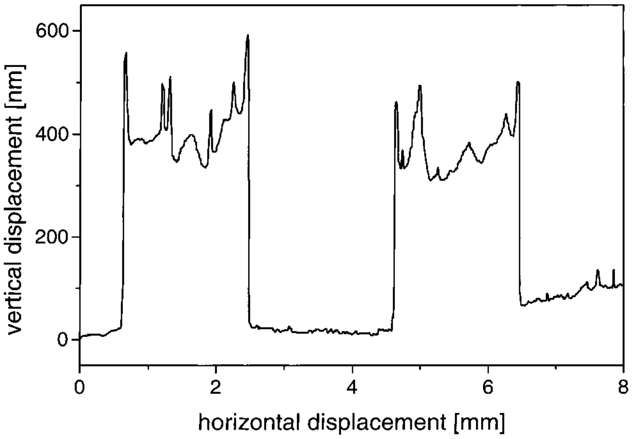


Figure 5. Surface profile of the pattern in Figure 4 investigated with a Dektak.

the substrate. After polymerization under the conditions mentioned above, the soluble part was removed with acetone or methylene chloride. The pattern is already visible. For further investigations scanning electron microscopy (SEM) photographs were taken after a 10 nm film of platinum was vacuum deposited onto the pattern.

The SEM picture at lower resolution shows the stripes of the organic material as dark lines whereas the ITO surface appears brighter gray (Figure 4a, left). On the right side the edge of the material of a different film is shown at a higher resolution (Figure 4b). The edge is well recognizable and, taking the rather simple patterning conditions into account, well developed.

In addition to the SEM investigations the pattern covered with platinum was investigated with a surface profiler in order to verify mechanically the pattern structure and dimensions. In Figure 5 the steps are clearly visible. The vertical distance of 2 mm is in agreement with the line width of the mask used. The rather sharp peaks on the polymeric surface detected with the surface profiler are caused by the measuring technique.

In conclusion, these experiments clearly demonstrate that it is possible to prepare cross-linked layers based on photopolymerizable hexaalkoxytriphenylenes.

LED Characteristics

Two-layer LEDs with the polymerizable triphenylene derivatives as HTL were investigated. The LEDs consisted of a 35 nm thick photopolymerized layer of triphenylene polymer on ITO which was prepared by spin-coating and subsequent photopolymerization under the conditions mentioned above. A 35 nm layer of Alq_3 is evaporated onto the UV-polymerized hole transport layer and subsequently 2 mm wide stripes of 200 nm of aluminum as cathode. The size of the emitting area was 0.16 cm^2. Luminescence was measured with a Minolta luminescence meter at room temperature under ambient conditions. The LEDs are operated in a continuous dc mode under forward bias with ITO as positive electrode. The maximum brightness obtained with the linear polymer made by photopolymerization of a layer of **1** was 130 cd/m^2 at a current density of 16 mA/cm^2 and an electric field of 2.6×10^6 V/cm (driving voltage approximately 18 V). The onset of the green emission from Alq_3 is at an electric field of 7.1×10^5 V/cm (5 V driving voltage). For a better comparison the characteristic brightness at 10 mA/cm^2 is 90 cd/m^2, and the characteristic current density at 100 cd/m^2 is 12 mA/cm^2. It should be noted that the maximum brightness of the diode made of photopolymerized **1** is 1 order of magnitude lower than a comparable device made by spin-coating of solution polymerized **1**.[15] This may be attributed to unoptimized preparation conditions and to the remaining monomer in the film.

To use triphenylenes as insoluble HTLs in two-layer organic LEDs, 35 nm thick films were prepared on ITO substrates. The used monomers are the three bisacrylates **2a**–**c** and both trisacrylates **3** and **4**. The thickness and preparation procedure for the electron transport/emitter layer Alq_3 and the top electrode from Al were same as in the case of the monoacrylate **1**.

The LED based on the photo-cross-linked bisacrylate **2a** starts to emit green light at an electric field of 4.3 ×

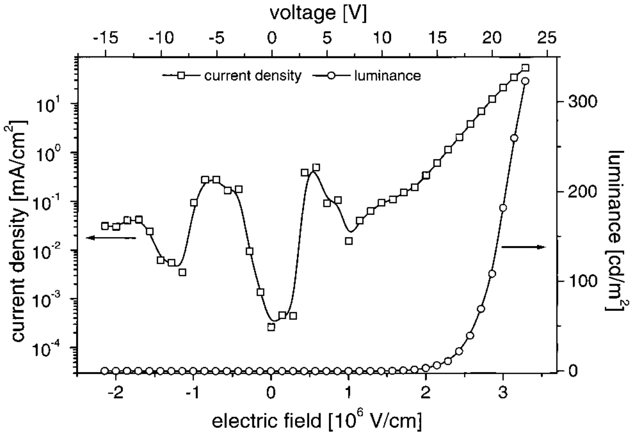


Figure 6. LED characteristic of a two-layer device with Alq_3 as emitting/electron transport layer and a cross-linked film of **3** as hole-transport layer ⟨ITO/**3** (35 nm)/Alq_3 (35 nm)/Al (200 nm)⟩.

Table 1. Comparison of the Characteristic Values of the Two-Layer LEDs with Cross-Linked Hole Transport Layers for 100 cd/m^2 and 10 mA/cm^2

compd	brightness [cd/m^2] at 10 mA/cm^2	current density [mA/cm^2] at 100 cd/m^2
2a	13	52
2b	8	87
2c	3	152
3	78	13
4	67	15

10^5 V/cm (3 V). Compared to the photopolymerized monoacrylate **1**, this onset field is rather low, but the current density in the LED of **2a** is much higher than in the device of **1**. A maximum brightness of 377 cd/m^2 is reached at an electric field of 1.7 × 10^6 V/cm and a current density of 220 mA/cm^2. Changing the substitution pattern from 3,6 (**2a**) to 2,7 (**2b**) had a rather minor influence on the LED behavior. No difference can be noted in the onset field. The LED of photo-cross-linked **2b** is a little less efficient than the one made of **2a**. At a maximum current density of 220 mA/cm^2 a maximum brightness of 185 cd/m^2 was achived with a network of **2b**. The device made from photopolymerized 2,6-substituted bisacrylate **2c** has a slightly higher onset field than that derived from **2a** and **2b**. The LED with cross-linked **2c** reaches a maximum brightness of 140 cd/m^2 at an electric field of 1.7 × 10^6 V/cm^2 and a current density of 272 mA/cm^2. Table 1 compares the characteristic LED values at 10 mA/cm^2 and 100 cd/m^2 of the two-layer devices with the cross-linked triphenylene films of **2a**−**2c**.

Figure 6 shows as an example the characteristics of a LED made from the trisacrylate **3**. The photo-cross-linked network of **3** in an identical device setup has a slightly higher onset field of 1.0 × 10^6 V/cm. At an electric field of 3.2 × 10^6 V/cm and a current density of 57 mA/cm^2, the maximum brightness of the green emission of 323 cd/m^2 was observed. The two-layer LED containing a network of **4** as HTL starts to emit green light at an electric field of 8.6 × 10^5 V/cm. The maximum brightness of 267 cd/m^2 is reached at an electric field of 3.2 × 10^6 V/cm and a current density of 91 mA/cm^2. In general, the diodes made from trisacrylates **3** and **4** can resist higher electric fields than the diodes of the bisacrylates **2**. This may be attributed to lower current densities. The characteristic data for the device—brightness at 10 mA/cm^2 and current density at 100 cd/m^2—are included in Table 1.

In summary, as shown in Table 1, the efficiency of the diodes containing the bisacrylates decreases from **2a** to **2c**. This is indicated by decreasing values for the brightness at 10 mA/cm^2 and increasing values for the current density at 100 cd/m^2. A correlation of the diode behavior of the bisacrylates to the varying substitution pattern is not obvious. Electronic reasons have to be excluded since the ether moieties at the active species are identical. Geometric considerations in terms of network formation and film-forming properties seem to be the most likely reason for the differences. In contrast, the diodes with cross-linked trisacrylate as hole transport layer have drastically reduced current densities at 100 cd/m^2 and, consequently, show much brighter luminescence at 10 mA/cm^2. The trisacrylate with pentyl side chains and a propyl spacer **3** shows a slightly better efficiency than the corresponding trisacrylate **4**. The values reached with the trisacrylate diodes are already in a range of 50−100 cd/m^2 at 10 mA/cm^2. As we wanted to demonstrate in this paper the principal function and utilization of cross-linkable hole transport layers in organic LEDs, no attempts were made to optimize the diode performance. Besides general considerations to improve the performance, such as more efficient electrodes than Al or complete handling under inert conditions, the quality of the hole transport layer could be improved by optimizing for example the polymerization conditions and by using monomer mixtures.

Conclusion

A series of hexaalkoxytriphenylenes having 1, 2, or 3 polymerizable acrylate units laterally attched have been synthesized and characterized. Conditions for photoinduced polymerization were evaluated, and the results demonstrate the formation of insoluble cross-linked layers from hexaalkoxytriphenylenes. Besides the proof by model reactions, the network formation was demonstrated by spectroscopic (UV, FT-IR), optical (SEM), and mechanical (surface profiler) means. A preparation of structured films by photopatterning using a negative resist technique with hole conducting triphenylenes was carried out. The insoluble cross-linked triphenylene layers were utilized as hole transport layers in two-layer LEDs with Alq_3. These devices show reasonable LED performance under the applied conditions.

Experimental Section

Materials. *2-[(3,6,7,10,11-Pentabutoxy-2-triphenylenyl)oxy]-ethyl Acrylate* ***1****: 1,2-Dibutoxybenzene* ***1a***. A mixture of 196.5 g (1.79 mol) of pyrocatechol, 538.3 g (3.93 mol) of 1-bromobutane, 298 g (2.16 mol) of K_2CO_3, and 0.5 g of 18-crown-6 in 300 g of 3-methyl-2-pentanone is refluxed for 48 h. After cooling to room temperature the mixture is diluted with 250 g of CH_2Cl_2 and filtered. The organic phase is separated and, after removal of the solvents, distilled. The fraction boiling around 117−120 °C at 1 mbar consist of **1a** and some monoether. This impurity is completely removed by washing with concentrated NaOH solution three times. Yield: 254.6 g (64.2%) of colorless liquid **1a**. ^1H NMR (250 MHz, $CDCl_3$): δ [ppm] = 6.9 (s, 4H, ar-H); 4.0 (t, 4H, OCH_2), 1.8 (m, 4H, OCH_2CH_2); 1.5 (m, 4H, CH_2CH_3); 1.0 (t, 6H, CH_3).

1,2-Dibutoxy-4-iodobenzene ***1b***. A mixture of 250 g (1.13 mol) of **1a**, 105.2 g (0.42 mol) of iodine, 44.5 g (0.25 mol) of HIO_3, 540 g of glacial acetic acid, 200 g of $CHCl_3$, 180 g of water, and 9 g of concentrated H_2SO_4 is stirred at 40 °C for 2.5 h. Then 500 mL of $CHCl_3$ and 300 mL of water are added; the organic phase is separated and extracted three times with 30 wt % Na_2SO_3 solution followed by one extraction with water. After drying with Na_2SO_4, the organic phase is filtered through a short silica column. Evaporating the solvent yields 367.6 g (93.9%) of pure **1b** as colorless liquid. ^{1}H NMR (250 MHz, $CDCl_3$): δ [ppm] = 7.2 (dd, 1H, ar-H_6); 7.1 (d, 1H, ar-H_2); 6.6 (d, 1H, ar-H_5), 4.0 (t, 4H, OCH_2), 1.8 (m, 4H, OCH_2CH_2); 1.5 (m, 4H, CH_2CH_3); 0.9 (t, 6H, CH_3).

*3,3′,4,4′-Tetrabutoxybiphenyl **1c***. **1b** (362.2 g, 0.82 mol) and Cu (43.4 g, 0.68 mol) are stirred under nitrogen at 200 °C for 6.5 h in an Ullmann apparatus and then cooled to 80 °C. At this temperature the mixture is carefully added to 500 mL of $CHCl_3$ and filtered through a short silica column. After evaporating the solvent and recystallization from methanol and ethanol, 99.6 g (43.3%) of **1c** is obtained as white crystals. ^{1}H NMR (200 MHz, $CDCl_3$): δ [ppm] = 7.0 (m, 4H, ar-H_2 and ar-H_6); 6.9 (d, 2H, ar-H_5), 4.0 (2xt, 8H, OCH_2), 1.8 (m, 4H, OCH_2CH_2); 1.5 (m, 4H, CH_2CH_3); 1.0 (t, 6H, CH_3); mp 91 °C.

*2-(2-Butoxyphenoxy)-1-ethanol **1d***. A mixture of 250 g (1.62 mol) of 2-(2-hydroxyethoxy)phenol, 490 g (3.58 mol) of 1-bromobutane, 247 g (1.79 mol) of K_2CO_3, 0.5 g of KI, 0.5 g of 18-crown-6, and 900 g of 3-methyl-2-pentanone is refluxed for 3 days. After cooling to room temperature the mixture is diluted with 600 mL of CH_2Cl_2, filtered, and washed with 400 mL of water. Evaporating the solvents and distillation at 0.1 mbar yields at 160 °C 216 g (63%) of **1d** as slightly yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ [ppm] = 6.9−6.8 (m, 4H, ar-H); 4.2−3.8 (m, 6H, ar-OCH_2CH_2OH and ar-OCH_2), 3.5 (t, 1H, OH), 1.8 (m, 2H, OCH_2CH_2); 1.5 (m, 2H, CH_2CH_3); 1.0 (t, 3H, CH_3).

*2-[(3,6,7,10,11-Pentabutoxy-2-triphenylenyl)oxy]-1-ethanol **1e***. **1c** (30 g, 68 mmol) and **1d** (42.7 g, 0.2 mol) are dissolved in 220 g of CH_2Cl_2, and 4 g of concentrated H_2SO_4 is added. The mixture is cooled to −10 °C, and 100 g (0.62 mol) of anhydrous $FeCl_3$ is added in small portions. After the last addition of $FeCl_3$ the mixture is stirred at −10 °C for 1.5 h and another hour at 10 °C. The reaction mixturet **1e** is precipitated in 1 L of chilled methanol and filtered off. The crude product **1e** is dissolved in CH_2Cl_2 and washed with hydroposphoric acid. The organic phase is separated, the solvent is evaporated, and **1e** is isolated by column chromatography on silica (eluent ethyl acetate/cyclohexane = 1:3) and finally recrystallized from ethanol. Yield: 24.2 g (54.8%) of pure **1e** as white crystals. ^{1}H NMR (250 MHz, $CDCl_3$): δ [ppm] = 7.8 (s, 4H, ar-H_5, ar-H_8, ar-H_9, ar-H_{12}); 7.7 (s, 2H, ar-H_1, ar-H_4), 4.3 (m, 2H, OCH_2CH_2-OH), 4.2 (m, 12H, OCH_2 and OCH_2CH_2OH), 3.7 (s, 1H, OH), 1.9 (m, 10H, OCH_2CH_2); 1.6 (m, 10H, CH_2CH_3); 1.0 (t, 15H, CH_3). Thermal transitions: ? D_h 134 i.

*2-[(3,6,7,10,11-Pentabutoxy-2-triphenylenyl)oxy]ethyl Acrylate **1***. **1e** (10 g, 15.4 mmol) 1.5 g (20.8 mmol) of acylic acid, 0.1 g of *p*-toluenesulfonyl chloride, and 0.1 g of hydroquinone are refluxed in 100 mL of toluene in a water separator. After 2 h another 2 g (27.8 mmol) of acrylic acid is added. After 3 days the mixture is cooled to room temperature, washed with 20% K_2CO_3 solution, and subsequently washed with water. The organic phase is dried with Na_2SO_4 and after evaporating the solvent passed over a silica column (eluent gradient: cyclohexane to cyclohexane/ethyl acetate = 9:1). Finally the product is recrystallized from ethanol to yield 5.6 g (52%) of pure **1**. ^{1}H NMR (250 MHz, $CDCl_3$): δ [ppm] = 8.0 (s, 1H, ar-H_1); 7.8 (s, 5H, ar-$H_{4,5,8,9,12}$); 6.5 (dd, 1H, $=CH_{2\,(trans)}$); 6.2 (dd, 1H, $CH=CH_2$); 5.9 (dd, 1H, $=CH_{2\,(cis)}$); 4.6 (t, 2H, $COOCH_2$), 4.5 (t, 8H, $COOCH_2CH_2$), 4.2 (t, 10H; $CH_2(CH_2)_2CH_3$); 1.9 (m, 10H, CH_2-CH_2CH_3); 1.6 (m, 10H, CH_2CH_3); 1.0 (t, 12H, CH_3). MS-EI: *m*/*z* 702, 75%, [$M^{\bullet+}$]; 99, 100%, $C_5H_7O_2$ (spacer acrylate). Thermal transitions: c 64 D_h 116 i.

*2,11-Bis(3-acryloxypropoxy)-3,6,7,10-tetrapentyloxytriphenylene **2a**, 2,7-Bis(3-acryloxypropoxy)-3,6,10,11-tetrapentyloxytriphenylene **2b**, and 2,6-Bis(3-acryloxypropoxy)-3,7,10,-11-tetrapentyloxytriphenylene **2c***. The bisacrylate **2a** is identical with the samples described in ref 20. **2b** and **2c** were prepared in analogy to **2a** from the corresponding dihydroxytriphenylene derivatives that are described in ref 20.

*2,7-Di(3-hydroxypropoxy)-3,6,10,11-tetrapentoxytriphenylene **2ba***. To a solution of 1.3 g (2.15 mmol) of 3,6,10,11-tetra(pentyloxy)-2,7-triphenylenediol and 0.89 g (6.46 mmol) of 3-bromo-1-propanol in 15 mL of 2-pentanone are added 8 g (58 mmol) of K_2CO_3 and 150 mg of KI with stirring, and the mixture is heated to 80 °C. After 5 h the mixture is cooled to room temperature, filtered to remove inorganic solids, and diluted with CH_2Cl_2. The organic phase is extracted with water, dried with Na_2SO_4, and evaporated. The product is purified by column chromatography (CH_2Cl_2/ethyl acetate = 8:1) followed by recrystallization from methanol to yield 0.84 g (54.3%) of white crystals of **2ba**. ^{1}H NMR (250 MHz, $CDCl_3$): δ [ppm] = 7.8−7.7 (3xs, 6H, ar-H); 4.4 (t, 4H, OCH_2-CH_2CH_2OH), 4.2 (t, 8H, OCH_2), 4.0 (t, 4H; CH_2OH); 2.9 (s, 2H, OH), 2.2−2.1 (m, 4H, CH_2CH_2OH); 2,0−1,9 (m, 8H, $CH_2(CH_2)_2$-CH_3; 1.6−1.4 (m, 16H, $(CH_2)_2CH_3$); 1.0 (t, 12H, CH_3). mp: 149 °C.

*2,6-Di(3-hydroxypropoxy)-3,7,10,11-tetrapentoxytriphenylene **2ca***. Preparation is analogous to **2ba**. Purified by column chromatography with CH_2Cl_2/ethyl acetate = 10:1 and precipitation from acetone in water (62.6%). ^{1}H NMR (250 MHz, $CDCl_3$): δ [ppm] = 7.8 (3xs, 6H, ar-H); 4.4 (t, 4H, OCH_2-CH_2CH_2OH), 4.2 (t, 8H, OCH_2), 4.0 (t, 4H; CH_2OH); 2.2−2.1 (m, 4H, CH_2CH_2OH); 2,0−1,8 (m, 8H, $CH_2(CH_2)_2CH_3$; 1.6−1.4 (m, 16H, $(CH_2)_2CH_3$); 1.0 (t, 12H, CH_3). Thermal transitions: ? D_h 108 i.

*2,7-Bis(3-acryloxypropoxy)-3,6,10,11-tetrapentyloxytriphenylene **2b***. A solution of 0.244 mL (3 mmol) of acryloyl chloride in 10 mL of CH_2Cl_2 is added in an argon atmosphere to a chilled solution of 0.72 g (1 mmol) of **2ba**, 0.522 mL (3 mmol) of diisopropylamine, and 70 mg of 2,6-*tert*-butyl-*p*-cresol in 20 mL of CH_2Cl_2. The mixture is allowed to warm to room temperature and is stirred for an additional 2 h before it is extracted with aqueous K_2CO_3 solution followed by extraction with water and drying of the organic phase with Na_2SO_4. The crude product is purified by column chromatography (CH_2Cl_2/ethyl acetate = 100:1) and recrystallization from ethyl acetate/ethanol = 1:1 to yield 696 mg (84.1%) of white crystals. ^{1}H NMR (250 MHz, $CDCl_3$): δ [ppm] = 7.8 (2xs, 6H, ar-H); 6.4 (dd, 2H, $=CH_{2\,(trans)}$); 6.1 (dd, 2H, $CH=CH_2$); 5.8 (dd, 2H, $=CH_{2\,(cis)}$); 4.5 (t, 4H, ar-$OCH_2CH_2CH_2O$), 4.3 (t, 4H, CH_2OCO); 4.2 (2xt, 8H, ar-OCH_2); 2.3 (m, 4H, CH_2CH_2OCO); 2,0−1,9 (m, 8H, $CH_2(CH_2)_2CH_3$; 1.6−1.4 (m, 16H, $(CH_2)_2CH_3$); 1.0 (t, 12H, CH_3). FD-MS: *m*/*z* 829.9, 100% [$M^{\bullet+}$]; mp 85 °C.

*2,6-Bis(3-acryloxypropoxy)-3,7,10,11-tetrapentyloxytriphenylene **2c***. Synthesis is analogous to **2b**, with a 76.8% yield. Column chromatography with CH_2Cl_2/ethyl acetate = 50:1. ^{1}H NMR (250 MHz, $CDCl_3$): δ [ppm] = 7.8 (2xs, 6H, ar-H); 6.4 (dd, 2H, $=CH_{2\,(trans)}$); 6.1 (dd, 2H, $CH=CH_2$); 5.8 (dd, 2H, $=CH_{2\,(cis)}$); 4.5 (t, 4H, ar-$OCH_2CH_2CH_2O$), 4.3 (t, 4H, CH_2OCO); 4.2 (2xt, 8H, ar-OCH_2); 2.4−2.2 (m, 4H, CH_2CH_2OCO); 2,0−1,9 (m, 8H, $CH_2(CH_2)_2CH_3$; 1.6−1.4 (m, 16H, $(CH_2)_2CH_3$); 1.0 (t, 12H, CH_3). FD-MS: *m*/*z* 829.8, 100% [$M^{\bullet+}$]; thermal transitions k 99 (D_h 65) i.

*2,6,10-Tributoxy-3,7,11-tris(2-acryloxyethoxy)triphenylene and 2,6,11-Tributoxy-3,7,10-tris(2-acryloxyethoxy)-triphenylene **4.*** *2-(2-Butoxyphenoxy)ethyl Acetate **4a***. **1d** (210 g, 1 mol) and acetic anhydride (102 g, 1 mol) are mixed, and 5 g of concentrated H_2SO_4 is added. The temperature rises to 109 °C. When the temperature starts decreasing, the mixture is heated on a water bath for an additional 2 h. The mixture is allowed to cool to room temperature and is poured onto crushed ice. A brown oil is separated, and the aqueous phase is extracted two times with CH_2Cl_2. The combined organic phases are washed with Na_2CO_3 solution and water and are dried with Na_2SO_4. After evaporating the solvent, the remaining oil is distilled at 0.1 mbar; 220 g (87%) of **4a** is collected at 169 °C as colorless liquid.

*2,6,10-Tributoxy-3,7,11-tris(2-acetoxyethoxy)triphenylene and 2,6,11-Tributoxy-3,7,10-tris(2-acetoxyethoxy)triphenylene **4b***. A 50 g (0.2 mol) sample of **4a** is dissolved in 220 g of CH_2Cl_2, and 5 g of concentrated H_2SO_4 is added. The mixture is cooled to −10 °C, and 64.4 g (0.4 mol) of anhydrous $FeCl_3$ is added in small portions. After the addition the mixture is stirred for 1.5 h at −10 °C and another hour at 10 °C. The crude product is precipitated in chilled methanol and washed with hydrophosphonic acid like described for **1e**. A 3.6 g (7%) sample of crude **4b** is obtained after evaporation of the solvent and not further purified.

2,6,10-Tributoxy-3,7,11-tris(2-hydroxyethoxy)triphenylene and 2,6,11-Tributoxy-3,7,10-tris(2-hydroxyethoxy)triphenylene ***4c***. **4b** (3.6 g, 4.8 mol), 3 g (53 mmol) of KOH, 15 g of water, and 180 g of ethanol are stirred with reflux for 3 days. After cooling the mixture to room temperature, 200 mL of water and 200 mL of CH_2Cl_2 are added; the organic phase is separated and subsequently dried with Na_2SO_4, and the solvent is removed. The remaining yellow solid is recrystallized from methanol to yield 2.1 g (89%) of **4c** as white crystals. mp: 202 °C.

2,6,10-Tributoxy-3,7,11-tris(2-acryloxyethoxy)triphenylene and 2,6,11-Tributoxy-3,7,10-tris(2-acryloxyethoxy)triphenylene ***4***. A 1.7 g (2.7 mmol) sample of **4c** and 0.5 g of di-*tert*-butyl-*p*-cresol are dissolved in 22 g of CH_2Cl_2 and 2.1 (21 mmol) of diisopropylamine. The mixture is cooled to 0 °C, and 1.4 g (15.5 mmol) of acryloyl chloride is added dropwise. The mixture is allowed to warm to room temperature and stirred for an additional 5 h. The solution is washed with 20% K_2CO_3 solution, dried with Na_2SO_4, and evaporated. The remaining solid is recystallized from ethanol to yield 1.6 g (75%) of pure trisacrylate **4** as isomeric mixture. ^{1}H NMR (250 MHz, $CDCl_3$): δ [ppm] = 8.0 (2xs, 3H, ar-H); 8.0 (2xs, 3H, ar-H); 6.5 (dd, 3H, $=\mathrm{C}H_{2\,(\mathrm{trans})}$); 6.2 (dd, 3H, $\mathrm{C}H{=}\mathrm{CH_2}$); 5.9 (dd, 3H, $=\mathrm{C}H_{2\,(\mathrm{cis})}$); 4.6 (t, 6H, $\mathrm{C}H_2$-OCO), 4.5 (t, 6H, ar-$\mathrm{OC}H_2\mathrm{CH_2O}$); 4.2 (m, 6H, $\mathrm{C}H_2\mathrm{(CH_2)_2CH_3}$); 1,9 (m, 6H, $\mathrm{C}H_2\mathrm{CH_2CH_3}$; 1.6 (m, 6H, $\mathrm{C}H_2\mathrm{CH_3}$); 1.0 (t, 9H, $\mathrm{C}H_3$). MS-EI: m/z 786, 75% [$M^{\bullet+}$]; 99, 100%, $C_5H_7O_2$ (spacer acrylate); thermal transitions k_1 90 k_2 95 D_h 104 i.

2,6,10- Tris(2-acryloxypropyloxy)-3,7,11-tripentyloxytriphenylene and 2,6,11-Tris(2-acryloxypropyloxy)-3,7,10-tripentyloxytriphenylene ***3***. The isomeric mixture was synthesized and purified in analogy to mixture **4**. ^{1}H NMR (250 MHz, $CDCl_3$): δ [ppm] = 7.9 (2xs, 6H, ar-H); 6.4 (dd, 3H, $=\mathrm{C}H_{2\,(\mathrm{trans})}$); 6.1 (dd, 3H, $\mathrm{C}H{=}\mathrm{CH_2}$); 5.8 (dd, 3H, $=\mathrm{C}H_{2\,(\mathrm{cis})}$); 4.5 (t, 6H, ar-$\mathrm{OC}H_2$-$\mathrm{(CH_2)_2O}$); 4.4 (t, 6H, $\mathrm{C}H_2\mathrm{OCO}$); 4.3 (m, 6H, $\mathrm{C}H_2\mathrm{(CH_2)_3CH_3}$); 2.3 (m, 6H, $\mathrm{OCH_2C}H_2\mathrm{CH_2O}$); 1,9 (m, 6H, $\mathrm{C}H_2\mathrm{(CH_2)_2CH_3}$; 1.6−1.4 (m, 12H, $\mathrm{(C}H_2\mathrm{)_2CH_3}$); 1.0 (t, 9H, $\mathrm{C}H_3$). MS-EI: m/z 870, 76% [$M^{\bullet+}$]; 113, 100%, $C_6H_9O_2$ (spacer acrylate); mp 77 °C.

Characterization. The molecular weight was determined by a Waters GPC system including a Waters 410 UV detector (254 nm) using THF as eluent and polystyrene standards. FT-IR spectra were recorded with a Bio-Rad spectrometer FTS-40. ^{1}H NMR spectra were measured with a Bruker AC 250. EI/MS spectra were measured with a Finnigan MAT 8500 with a MAT 112 S Varian. UV spectra were recorded using a Hitachi spectrometer U-3000. SEM pictures were taken with a Joel 840-A electron microscope.

LED Device Preparation. Indium−tin oxide (ITO)-coated glass with a sheet resistance below 30 Ω/cm^2 (Merck-Balzers Co.) was used as substrate for LEDs. The thickness of the ITO layer was 120 nm. Cleaning of the ITO glass includes sonication steps in $CHCl_3$ and ethanol.

Evaporation of the Alq_3 layers and the aluminum electrode (200 nm) was done at a pressure of 1×10^{-5} mbar and a rate of 2 Å/s in Balzers PLS 500 evaporation equipment. The size of the emitting areas was 0.16 cm^2.

Spin-coating was done from 1 to 1.5 wt % THF solutions with a Convac 1001 spin-coater controlled by a Siemens Coros OP15 at room temperature under red light.

Irradiation was done with a Xe 150 W lamp in a AMKO A1020 housing connected to a AMKO LPS210 power supply on a Störtronic hot plate PZ 28-2T.

LED Device Characterization. Electroluminescence spectra (EL) and photoluminescence spectra (PL) were recorded on a Shimadzu RF-5301 PC fluorescence spectrophotometer at room temperature. For the PL measurements Alq_3 was vapor deposited onto a quartz glass substrate.

Thickness and surface profile of patterned films were measured by a Dektak 3030 St surface texture profiler.

Luminance was measured with a Minolta luminance meter LS 100. The current−voltage measurements were PC-controlled and carried out using a Keithley 2000 digital multimeter with a Grundig PN 300 power supply with simultaneous detection of the electroluminescence by the Minolta luminance meter. All measurements were performed at ambient conditions in air.

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References and Notes

(1) (a) Tang, C. W.; VanSlyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913. (b) Tang, C. W.; VanSlyke, S. A.; Chen, C. H. *J. Appl. Phys.* **1989**, *65*, 3610.

(2) (a) Adachi, C.; Tsutsui, T.; Saito, S. *Appl. Phys. Lett.* **1990**, *56*, 799. (b) Adachi, C.; Nagai, K.; Tamoto, N. *Appl. Phys. Lett.* **1995**, *66*, 2679.

(3) Kido, J.; Nagai, K.; Okamoto, Y.; Skotheim, T. *Appl. Phys. Lett.* **1991**, *59*, 2760.

(4) (a) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539. (b) Bradley, D. D. C. *Adv. Mater.* **1992**, *4*, 756. (c) Braun, D.; Heeger, A. J. *Appl. Phys. Lett.* **1991**, *58*, 1982. (d) Greenham, N. C.; Moratti, S. C.; Bradley, D. D. C.; Friend, R. H.; Holmes, A. B. *Nature* **1993**, *365*, 628. (e) Friend, R. *Synth. Met.* **1992**, *51*, 357.

(5) (a) Leising, G. *Phys. Bl.* **1993**, *49*, 510. (b) Forrest, S. R.; Burrows, P. E.; Thompson, M. E. *Laser Focus World* **1995**, *February 99*. (c) Bulovic, V.; Gu, G.; Burrows, P. E.; Forrest, S. R.; Thompson, M. E. *Nature* **1996**, *318*, 29.

(6) Buchwald, E.; Meier, M.; Karg, S.; Pösch, P.; Schmidt, H.-W.; Strohriegl, P.; Riess, W.; Schwoerer, M. *Adv. Mater.* **1995**, *7*, 839.

(7) Herold, M. Dissertation, Bayreuth, 1997.

(8) Herold, M.; Gmeiner, J.; Drummer, C.; Schwoerer, M. *J. Mater. Sci.* **1997**, *32*, 5709.

(9) See for example: (a) Fouassier, J.-P. *Photoinitiation Photopolymerization and Photocuring*; Carl Hanser Verlag: Munich, 1995. (b) Pappas, S. P. *UV Curing Science and Technology*; Marketing Corp.: Norwalk, CT, 1985; Vol. II Technology.

(10) Bellmann, E.; Shaheen, S. E.; Thayumanavan, S.; Barlow, S.; Grubbs, R. H.; Marder, S. R.; Kippelen, B.; Peyghambarian, N. *Chem. Mater.* **1998**, *10*, 1668.

(11) Adam, D.; Schuhmacher, P.; Simmerer, J.; Häussling, L.; Paulus, W.; Siemensmeyer, K.; Etzbach, K.-H.; Ringsdorf, H.; Haarer, D. *Adv. Mater.* **1995**, *7*, 276.

(12) Simmerer, J.; Glüsen, B.; Paulus, W.; Kettner, A.; Schuhmacher, P.; Adam, D.; Etzbach, K.-H.; Siemensmeyer, K.; Wendorff, J. H.; Ringsdorf, H.; Haarer, D. *Adv. Mater.* **1996**, *8*, 815.

(13) Adam, D.; Haarer, D.; Closs, F.; Funhoff, D.; Siemensmeyer, K.; Schuhmacher, P.; Ringsdorf, H. *Ber. Bunsen-Ges. Phys. Chem.* **1993**, *97*, 1366.

(14) (a) Christ, T.; Glüsen, B.; Greiner, A.; Kettner, A.; Sander, R.; Stümpflen, V.; Tsukruk, V.; Wendorff, J. H. *Adv. Mater.* **1996**, *9*, 48. (b) Christ, T.; Stümpflen, V.; Wendorff, J. H. *Makromol. Chem. Rapid Commun.* **1997**, *18*, 93.

(15) Bacher, A.; Bleyl, I.; Erdelen, C. H.; Haarer, D.; Paulus, W.; Schmidt, H.-W. *Adv. Mater.* **1997**, *9*, 1031.

(16) Henderson, P.; Ringsdorf, H.; Schuhmacher, P. *Liq. Cryst.* **1995**, *18*, 191.

(17) Boden, N.; Bushby, R. J.; Cammidge, A. N. *J. Chem. Soc., Chem. Commun.* **1994**, 465.

(18) Wirth, H. O.; Königstein, O.; Kern, W. *Liebigs Ann. Chem.* **1960**, *634*, 48.

(19) Späth, E.; Gibian, K. *Monatsh. Chem.* **1930**, *55B*, 342.

(20) Closs, F.; Häussling, L.; Henderson, P.; Ringsdorf, H.; Schuhmacher, P. *J. Chem. Soc., Perkin Trans.* **1995**, *1*, 829.

(21) (a) Davison, W. H. T.; Bates, G. R. *J. Chem. Soc.* **1953**, 2607. (b) Walton, W. L.; Hughes, R. B. *J. Am. Chem. Soc.* **1957**, *79*, 3985.

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