A New Polymeric Triarylamine and Its Use as a Charge Transport Layer for Polymeric LEDs

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ABSTRACT: A new hole injecting polymer for an electroluminescent element was prepared by radical polymerization of a methacrylate monomer that contains an *N*′-biphenyl-*N*,*N*-diphenylamine unit as a pendent side chain. Cyclic voltammetry of the polymer coated on an ITO electrode shows a chemically irreversible oxidation at 1.2 V. Subsequent cycles reveal that the newly formed species is electrochemically stable. The polymer was used as both an electroluminescent layer and a hole injection layer in single- and double-layered devices, respectively. The double-layered device using ITO as the anode, Al as the cathode, and poly[methyl(2-(1-pyrenyl)ethyl)siloxane] as the electroluminescent layer gave bright blue-green light with a maximum brightness level of 168 cd/m^2 and an internal quantum efficiency of 0.20%.

Introduction

Over 30 years ago, electroluminescence (EL) was observed from a crystal of anthracene.[1,2] Several years following the initial discovery of organic electroluminescence, Tang,[3−7] Saito,[8−14] and others[15,16] reported on light-emitting diodes (LEDs) composed of vapor-deposited fluorescent dyes and polymeric films doped with fluorescent dyes. They also reported the fabrication of multilayered devices utilizing a hole transport layer (HTL), an electron transport layer (ETL), and an emitting layer. The HTL and ETL are physically and chemically distinct layers whose intrinsic properties facilitate the injection and transport of holes and electrons, respectively. In addition, the HTL is a poor carrier for electrons, while the ETL is a poor carrier for holes, which therefore helps confine hole and electron recombination to the emitting layer. HTLs and the ETLs are sometimes referred to in general terms as charge injection/confinement layers. While molecular LEDs were being developed, Friend and co-workers discovered that conjugated polymers such as poly(phenylenevinylene) could also be used as an emitting layer in an LED.[17,18] This discovery initiated the burgeoning field of polymer LEDs, and since then numerous studies on conjugated polymers, segmented polymers, and polymer blends have demonstrated this phenomenon.[19−31,37,38]

Since these initial discoveries, a substantial effort has been directed toward improvement of device lifetime and efficiency. In this regard, incorporation of charge confinement/injection layers into the LED design was found to be of great value in both molecular and polymeric systems.[14,19,20] For example, electron injection layers comprising an oxadiazole dispersed in poly(methyl methacrylate),[19] cyano-substituted poly(*p*-phenylenevinylene),[20] or hole injection layers comprising poly(9-vinylcarbazole)[21,22] have dramatically improved the performance characteristics of polymeric LEDs leading to internal efficiencies of up to 4% with a calcium cathode.

Recently, we reported on the development of a new class of polymers which exhibit electroluminescence with indium tin oxide, ITO, and Al electrodes.[32] These polymers comprise a flexible polymer backbone having a pendent fluorescent chromophore on every, or nearly every, repeat unit. We additionally reported on side chain copolymers composed of an emitting and a charge carrying species. LEDs prepared from these materials performed reasonably well with a maximum efficiency of 0.01%. The incorporation of an ETL with one of the systems significantly improved device performance, e.g., efficiency of ~0.1%, brightness = 173 cd/m^2.

Incorporation of an HTL was the next logical step in the development of these systems. It was anticipated that device efficiency should improve by confining hole and electron recombination to the emitting layer. The literature indicates that tetraphenylbenzidine, TPD, and other related triphenylamines have been by far the most widely used HTLs in the preparation of organic LEDs.[6,11,13] These materials form colorless, amorphous films which can be readily prepared by vapor deposition techniques. It would be desirable from a processing standpoint, however, to be able to form an HTL using standard solvent coating techniques. Hence, we prepared a polymer with pendent triarylamine units, and in this report we discuss the redox and the electroluminescent properties of this polymer and its utilization as an HTL in a multilayer EL device using a side chain polymer as the emitting layer.

Experimental Section

Materials. All reagents were supplied by Aldrich Chemical Co. unless stated otherwise. All solvents, e.g., methylene chloride, ethyl acetate, hexanes, and acetonitrile, were purchased from J. T. Baker, Inc. Acetonitrile was distilled from CaH_2 before use, while the other solvents were used as received. Tetrabutylammonium tetrafluoroborate, TBATFB, electrometric grade, from Southwestern Analytical Chemical, Inc., and isocyanatoethyl methacrylate, from Monomer-Polymer Laboratories, were both used as received.

Synthesis. Preparation of 4-(*N*,*N*-Diphenylamino)-4′-nitrobiphenyl (I). The 4-(*N*,*N*-diphenylamino)-4′-nitrobiphenyl was prepared by the reaction of 4-iodo-4′-nitrobiphenyl with 1 equiv of diphenylamine following the procedure of Gauthier and Fréchet.[33] The nitro compound was isolated by column chromatography (silica gel, hexane/ethyl acetate). The resulting orange-yellow solid was recrystallized from 2-propanol to give **I** in 68% yield (mp 149−150 °C). ^{1}H NMR ($CDCl_3$): δ 7.15 (8H, multiplet, aromatic H), 7.4 (4H, multiplet, aromatic H), 7.5 (2H, doublet, aromatic H), 7.95 (2H, doublet, aromatic H), 8.35 (2H, doublet, aromatic H). ^{13}C NMR ($CDCl_3$): δ 123.21, 124.59, 124.77, 125.80, 127.66, 128.93, 130.32, 132.10, 147.29, 147.46, 147.99, 149.64. IR (KBr): 3050,

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1600, 1510, 1495, 1350, 1295, 1220, 1190, 1120, 805, 790, 755, 675 cm^{-1}. Mass spectroscopy m/z (FAB): 367 (m + 1). UV (CH_2Cl_2): $\lambda_{max} = 296$ nm ($\epsilon = 24\,400$), 406 nm ($\epsilon = 17\,300$).

Preparation of *N*-(4-(*N*,*N*-Diphenylamino)biphenylyl-4′)-*N*′-(2-(methacryloyloxy)ethyl)urea (II). 4-(*N*,*N*-Diphenylamino)-4′-nitrobiphenyl, 2.0 g, was converted to the corresponding 4-(*N*,*N*-diphenylamino)-4′-aminobiphenyl by room temperature catalytic hydrogenation in THF, 30 mL, using 0.400 g of palladium on carbon (10% palladium content) in a hydrogen atmosphere. After complete reduction of the nitro compound, as indicated by TLC (silica gel, hexanes/methylene chloride, 4/1), the reaction mixture was filtered through a pad of Celite to remove the catalyst. Solvent was removed *in vacuo*, yielding the crude 4-(*N*,*N*-diphenylamino)-4′-aminobiphenyl. The crude product was reacted directly with isocyanatoethyl methacrylate (IEM), 1.2 equiv assuming 100% yield for the amine, in THF overnight at room temperature. The resulting IEM derivative was purified by column chromatography (methylene chloride/ethyl acetate) followed by recrystallization from acetonitrile to yield the methacrylate as a white crystalline solid in 75% yield, mp 158−159 °C. ^1H NMR ($CDCl_3$): δ 1.8 (3H, singlet, $-C(CO)CH_3$), 3.4 (2H, multiplet, $NHCH_2CH_2$), 4.2 (2H, triplet, CH_2CH_2O), 5.45 (1H, singlet, $(CO)C(CH_3){=}CHH$ cis to CH_3), 5.65 (1H, triplet (broad) NH), 6.1 (1H, singlet, $(CO)C(CH_3){=}CHH$ trans to CH_3), 7.0−8.75 (19H, multiplet, aromatic H and NH). Exact mass spectroscopy gave a mass of 491.2265 g/m. UV (CH_2Cl_2): $\lambda_{max} = 268$ ($\epsilon = 12\,200$), 328 ($\epsilon = 22\,500$).

Preparation of Poly(*N*-(4-(*N*,*N*-diphenylamino)biphenylyl-4′)-*N*′-(2-(methacroyloxy)ethyl)urea) (III). Monomer **II**, *N*-(4-(*N*,*N*-diphenylamino)biphenylyl-4′)-*N*′-(2-(methacroyloxy)ethyl)urea, 1.0 g, was charged into a flame-dried, argon-flushed reaction vessel equipped with a magnetic stirrer, a reflux condenser, and a rubber septum cap. While purged with argon, THF (Aldrich Sure Seal) was added in sufficient amount to make a 10 wt % solution of the monomer. The polymerization was run under a blanket of argon for 48 h at 60 °C using AIBN, 0.010 g, as the radical initiator. The solution was then cooled to room temperature and precipitated into methanol (20 mL of methanol/mL of polymer solution). The polymer was collected by vacuum filtration, redissolved in chloroform, and reprecipitated in methanol. After filtration and washing the solid polymer with methanol, it was dried under vacuum to yield the polymer as a white solid, $T_g = 185$ °C. IR (KBr): 3400, 3150, 2980, 1735, 1675, 1600, 1530, 1495, 1350, 1295, 1220, 1190, 820, 755, 675 cm^{-1}. UV (CH_2Cl_2): $\lambda_{max} = 286$ nm ($\epsilon = 12\,200$), 328 nm ($\epsilon = 22\,500$). Photoluminescence spectra of a thin film coated on a quartz plate reveals a λ_{em} at 405 nm with $\lambda_{ex} = 375$ nm. GPC analysis of this polymer was done in DMF vs polystyrene standards, $M_w = 2.75 \times 10^6$, $M_n = 1.14 \times 10^6$.

Preparation of Poly[methyl(2-(1-pyrenyl)ethyl)siloxane] (IV). A flame-dried, argon-flushed reaction vessel equipped with a magnetic stirrer, a reflux condenser, and an argon gas inlet/outlet adapter was charged with 0.16 g of poly(methylhydrosiloxane), 85 cs (Petrarch PS 122), 0.606 g of 1-vinylpyrene, 0.0022 g of chloroplatinic acid, and 10 mL of dry toluene. The resultant reaction mixture was stirred and heated at about 75 °C, under an argon atmosphere for about 1 week. The reaction was monitored by the disappearance of vinylpyrene using TLC (silica gel, hexanes) and by infrared spectroscopy monitoring the disappearance of the Si−H stretch at 2200−2100 cm^{-1}. When the Si−H stretch had completely disappeared in the infrared spectrum, the reaction temperature was lowered to 55 °C and 5 drops of 1-hexene was added to the reaction mixture. Heating continued for an additional 4 h to ensure complete consumption of the Si−H functional group. The reaction mixture was then cooled to room temperature and precipitated into hexanes. The solid polymer was recovered by filtration, washed in a Soxhlet apparatus using methanol, and finally dried in a vacuum oven at room temperature for 24 h. The molecular weight of the polymer, as measured by GPC in THF against polystyrene standards, was $M_w = 1.84 \times 10^4$, $M_n = 6.2 \times 10^3$. UV ($CHCl_3$): $\lambda_{max} = 268$ nm ($\log \epsilon = 4.2$), 278 nm (4.35), 330 (4.25), 348 nm (4.30).

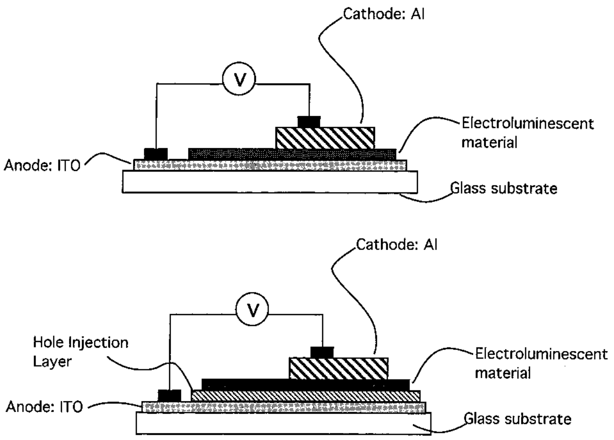


Figure 1. Schematic diagrams for (a) a single-layer device and (b) a double-layer device with a hole injection layer.

Techniques. Photoluminescence spectra were obtained on a Spex Fluorolog 2 using depolarized light, while the UV−vis spectra were recorded using a Hewlett Packard 8452a diode array spectrophotometer. The EL devices were characterized using a Hewlett Packard 4145B semiconductor parameter analyzer. The electroluminescence spectra were recorded using a JY CP2000 spectrograph equipped with a Prism Research photodiode array. Electroluminescence measurements were performed under ambient conditions.

Cyclic voltammograms were obtained by means of a Bioanalytical Systems BAS100W voltammetric analyzer and a Digital equipment Corp. DEC pc 433dxLP computer. Electrolysis was carried out using a three-electrode cell in acetonitrile containing 0.1 M of tetrabutylammonium tetrafluoroborate (TBATFB) as the electrolyte. A platinum wire functioned as the auxiliary electrode, while the reference electrode was a silver/silver nitrate electrode composed of a silver wire in acetonitrile, 0.010 M in silver nitrate and 0.100 M in TBATFB. The working electrode was the polymer-coated 10 Ω ITO glass. Dry nitrogen was bubbled through the cell for 20 min prior to electrolysis. Electrolysis was run at room temperature (21 °C).

Thin films of **III** for cyclic voltammetry, photoluminescence, and absorbance were obtained by spin casting a chloroform solution (1% by weight of the triarylamine polymer **III**), at 1000 rpms for 30 s. Prior to coating the polymer solution, the ITO and quartz substrates were ultrasonically cleaned in chloroform and acetone for 5 min, respectively, followed by drying in an N_2-purged oven for 30 min at 75 °C.

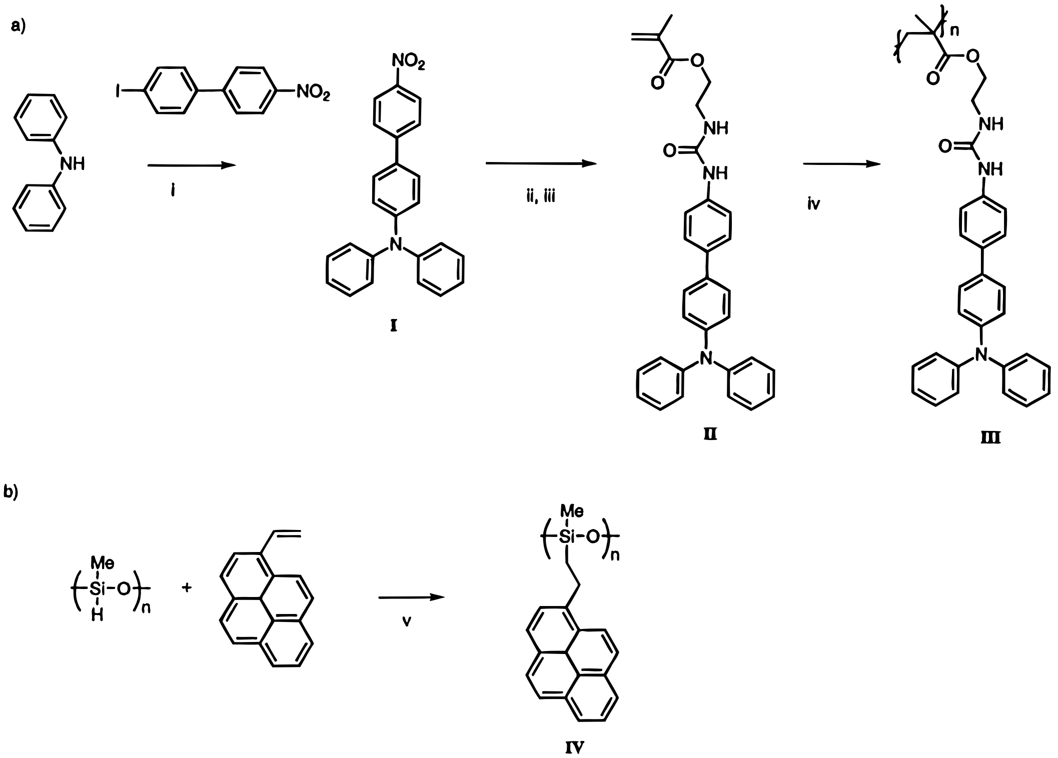
The devices for electroluminescence experiments were prepared by spin coating the appropriate polymer solution onto clean ITO which was previously subjected to an Ar/O_2 plasma and then surface treated with a 10% solution of 1,1,1,3,3,3-hexamethyldisilazane (HMDS) in chloroform.

The EL cells employed in this study were of two designs. One was a single layer of polymer sandwiched between the anode (ITO) and the cathode (Al), Figure 1a. The second consisted of two polymer layers consecutively coated onto the ITO electrode followed by the Al cathode, Figure 1b. A 0.5% chloroform solution of **III** and a 1.0% toluene solution of **IV** were used to prepare the respective polymer layers. After coating the polymer solution, the sample was baked in an N_2-purged oven at 70 °C for 1 h. In the cases where a second polymer layer was desired, it was deposited onto the first layer followed by a postbake at 70 °C for 1 h. Aluminum electrodes, 0.11 cm^2 dots, with a thickness of 400 nm were thermally evaporated at a pressure of 10^{-6} Torr, resulting in the final device structure.

Results and Discussion

Synthesis. The method for preparing polymer **III** is outlined in Scheme 1. First, *N*,*N*-diphenylamine was coupled with 4-nitro-4′-iodobiphenyl using the procedure of Gauthier and Fréchet.[33] The resulting 4-(*N*,*N*-diphenylamino)-4′-nitrobiphenyl, **I**, which was recovered after

Scheme 1. Synthesis of Electroactive (a) Triarylamine Polymer III and (b) Siloxane−Pyrene Polymer IV[a]



[a] i. Refluxing *o*-dichlorobenzene with 18-crown 6, Cu powder and K_2CO_3. ii. H_2, 10% Pd/C in THF. iii. IEM, THF. iv. AIBN THF, 60 °C. v. Chloroplatinic acid in toluene 75 °C.

chromatography in good yield, was converted to the 4-(*N*,*N*-diphenylamino)-4′-aminobiphenyl by catalytic hydrogenation (ii). The amino compound was not isolated but was directly converted to monomer **II** by reaction with isocyanatoethyl methacrylate (iii). Following chromatography and recrystallization from acetonitrile, monomer **II** was radically polymerized using AIBN as an initiator in THF at 65 °C (iv). After 45 h, the viscous solution was precipitated into methanol, washed with methanol, and dried under vacuum, yielding the polymer as a white fluffy solid.

EL polymer **IV** was prepared by a hydrosilylation reaction of 1-vinylpyrene with poly(methylhydrosiloxane) using chloroplatinic acid as the catalyst. After the reaction was complete, the polymer solution was precipitated into hexanes, filtered, washed with methanol, and dried under vacuum.

Cyclic Voltammetry. CV is a routine characterization technique for determining the redox properties of organic and polymeric materials. Compton et al. have demonstrated that this technique is applicable to electrodes modified with an electroactive polymer.[34] In our system electrolysis was carried out using a three-electrode cell in acetonitrile containing 0.100 M of tetrabutylammonium tetrafluoroborate (TBATFB) as the electrolyte. A platinum wire functioned as the auxiliary electrode, while a silver/silver nitrate electrode which consisted of a silver wire in acetonitrile, 0.010 M in silver nitrate and 0.100 M in TBATFB, was used as the reference electrode. ITO glass coated with a thin layer of the triarylamine polymer was used as the working electrode. A typical cyclic voltammogram corresponding to the oxidation of an ITO electrode coated with **III** recorded at 100 mV s^{-1} is shown in Figure 2. The initial oxidation/reduction cycle demonstrated in Figure 2a shows a large oxidation wave with a maximum electropotential (E_p) at 1.2 V and two single electron reduction waves with peaks at 0.84 and 0.53 V. Subsequent cycles, Figure 2b, revealed that the first oxidation wave at 1.2 V was not reversible and that after the initial redox cycle, the film displayed two reversible one-electron processes. The E_p values for the first and second peaks were at 0.71 and 1.03 V, respectively, while the two single-electron reduction reactions remained unchanged.

The redox behavior exhibited by this system is indicative of a chemically irreversible process which leads to a new electrochemically stable species. This type of behavior for molecular and polymeric triarylamines is well documented. Both Adams[35] and Ambrose[36] have demonstrated an oxidative coupling in molecular aromatic amines, while Compton has shown oxidative coupling in a polymeric system.[34] Their proposed mechanism is an irreversible oxidative coupling to form a bis(benzidine) moiety which then undergoes a reversible two-electron oxidation. In a polymeric system, the oxidative coupling should cross-link the polymer through the pendent triarylamine units, rendering the materials insoluble. Indeed, coatings of polymer **III** become insoluble after the first redox cycle.

Electroluminescence. Single-Layered Device. The light−current vs voltage, i.e., *LIV*, characteristics of a single-layer device consisting of an ITO anode, an aluminum cathode, and a polymer layer composed of either the triarylamine polymer **III**, Figure 3a, or the EL polymer **IV**, Figure 3b, are shown in Figure 3. The polymer layer thicknessess for the two devices were 60 nm for polymer **III** and 40 nm for polymer **IV**. When operated under a forward bias, electropotential across the device where the ITO electrode was the anode and the Al electrode was the cathode, both devices show typical rectifying behavior. For polymer **III**, current injection started at a bias of ~8 V and increased rapidly with an increase in bias up to 20 V, while light emission

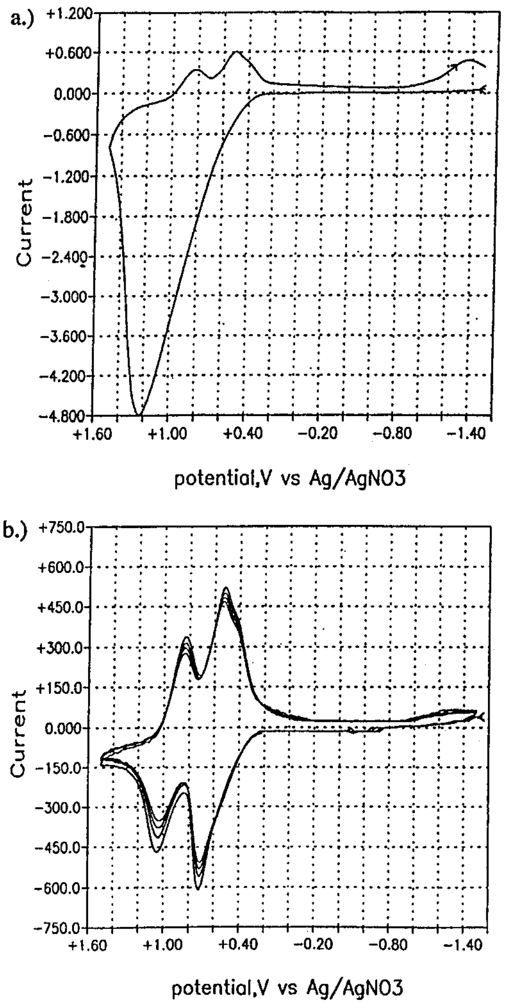


Figure 2. Cyclic voltammogram of polymer **III** coated on 10 Ω ITO: (a) first cycle; (b) second and subsequent cycles.

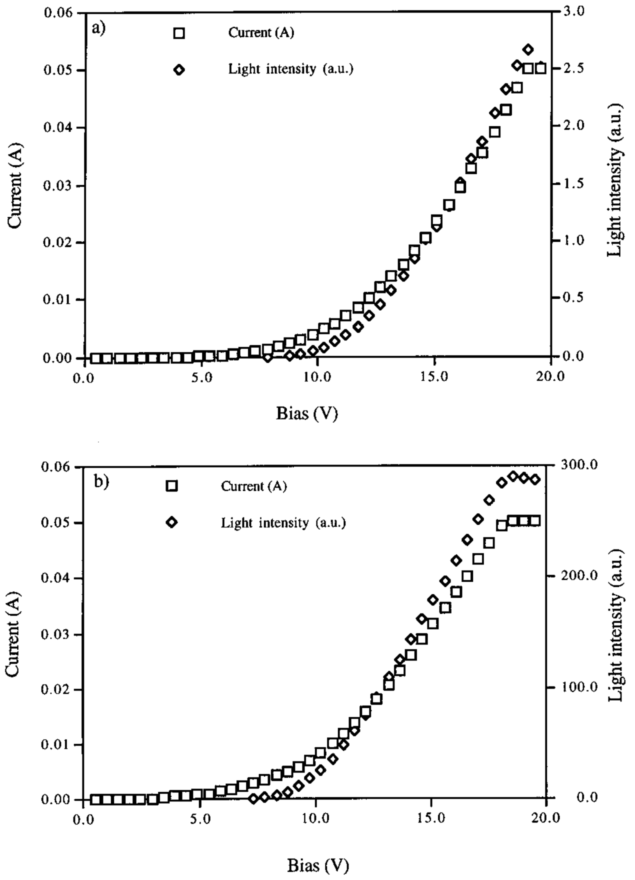


Figure 3. Current and light emission vs voltage for the single-layer LEDs prepared using (a) polymer **III** and (b) polymer **IV**.

originated at a bias of ~11 V. Similar behavior was observed for the siloxane pyrene system, **IV** (Figure 3b), in which current injection started at a bias of ~5 V and increased with increasing bias up to 20 V and light emission began at a bias of 7−8 V.

Further examination of the two single-layer devices presented shows that there is some leakage current at low voltage, as indicated by the discrepancies between the turn on voltage for current injection and light emission. This difference, albeit small, is indicative of some imbalance in the injection of opposite charges at the two electrodes. For the ITO/**IV**/Al device current starts to be injected at ~5 V, while light is not emitted until the bias reaches ~8 V. The slight imbalance suggests that the incorporation of a charge confinement layer, such as **III,** in the device structure could improve device performance.

The light vs current, i.e., *LI*, curves for the single-layer devices are given in Figure 4. The *LI* curve, a measure of the light emitted from the device as a function of the current flowing through the device, can be used to determine the efficiency of the diode. In our case, we collect the raw data as a plot of the photocurrent vs device current to determine diode efficiency. The photocurrent is a measure of the light detected by a calibrated photodiode and is directly proportional to the intensity of the light emitted from the diode through the ITO glass plate. The device fabricated from polymer **III** gave a maximum of 2.5 nA of photocurrent, which corresponds to a brightness of <0.1 cd/m^2. On the other hand, polymer **IV** started to emit at a bias of ~8 V, and the intensity of this emission increased with increasing bias, up to 20 V. A photocurrent maximum of 290 nA was attained, corresponding to a brightness of ~7 cd/m^2 at 497 nm and an *internal* efficiency of 0.0026%. It should be noted that the efficiency calculation takes into account losses of light due to internal reflection.

Two-Layer Device. The fact that polymer **III** is easily oxidized in a CV experiment when coated on an ITO electrode suggests that it may be useful as a hole injection material for an electroluminescent element. For example, we prepared a two-layer device which comprised an ITO electrode coated sequentially with **III** followed by polymer **IV**. After drying, 400 nm thick Al electrodes were deposited to yield the final device structure (Figure 1b). The two polymer layers had a combined thickness of 80 ± 5 nm.

The LIV character of a typical ITO/**III**/**IV**/Al device is shown in Figure 5. The two-layered device demonstrates rectifying behavior and turns on at 7 V. As the bias increases, the *IV* curve shows a slight discontinuity in the range of 8−11 V. Above 11 V the current increases rapidly with increasing bias up to 20 V.

The *LV* curve for the two-layer device shows that light emission starts at ~11 V, and the intensity of this emission increased with increasing bias up to 20 V. The difference in the turn on voltage for the current and the light emission is ~4 V, if one discounts the discontinuity in the *IV* curve. At this time, we have no explanation for this discontinuity. It could be the result of normal leakage current or impurities which act as charge carriers which become saturated at the higher voltage where emission begins.

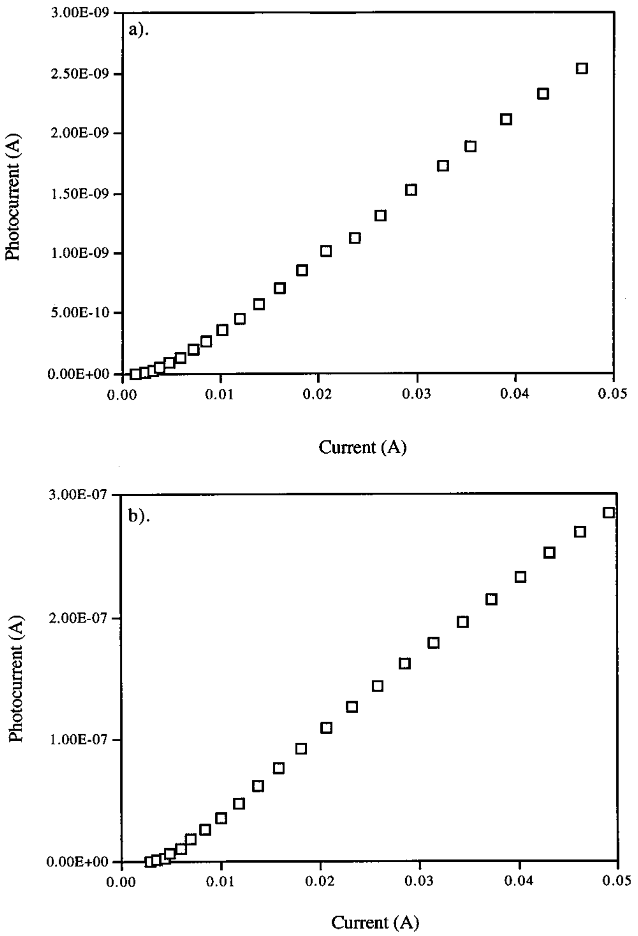


Figure 4. Photocurrent vs current for the single-layer LEDs prepared using (a) polymer **III** and (b) polymer **IV**.

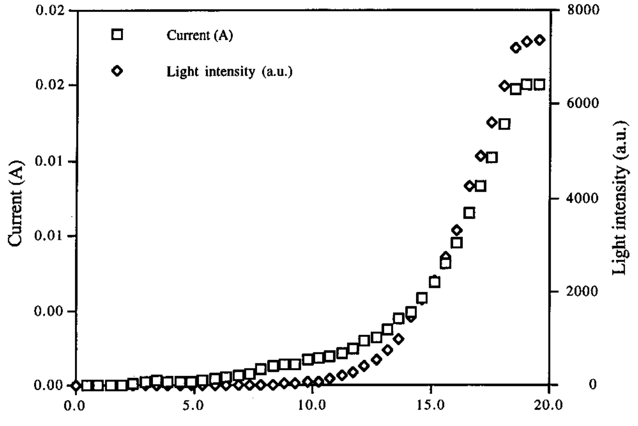


Figure 5. Current and light emission vs voltage for the two-layer diode (ITO/**III**/**IV**/Al).

A plot of L vs I for the ITO/III/IV/Al device is given in Figure 6. Light emission increases linearly with increasing current. A maximum intensity of 168 cd/m^2 was attained along with an internal efficiency of 0.20%.

A comparison of the EL characteristics of the single-layered device with the double-layered device demonstrates a dramatic improvement in device performance. Device brightness and efficiency were improved by a factor of 24 and ~100, respectively. These improvements in performance suggest that polymer **III** has the ability to act as a hole injection layer (electron blocking layer), confining charge recombination to the EL layer, polymer **IV**. The efficiency and brightness for the two-layer device which utilizes an Al cathode, is comparable to, if not greater than, other "blue" emitting devices reported.[37,38] It should be noted that some of the latter use Ca, a low work function metal, as the cathode.

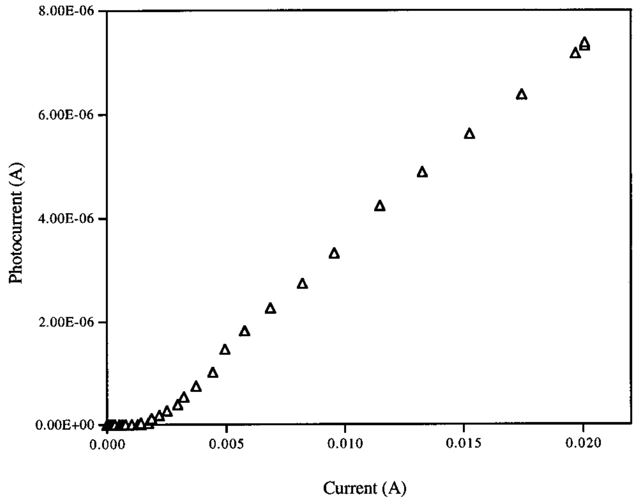


Figure 6. Photocurrent vs current for the two-layer diode (ITO/**III**/**IV**/Al).

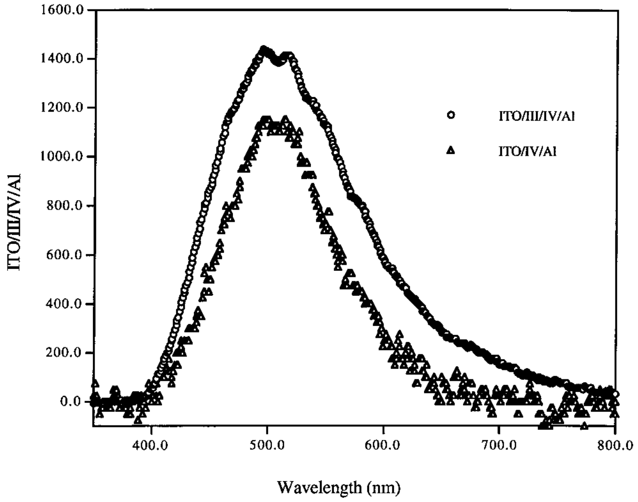


Figure 7. Normalized electroluminescence spectra for the single-layer LED using **IV** as the emitting layer, △, and the double-layer device using **III** as a HTL and **IV** as the emitting layer, ○.

The EL spectrum for the two-layered device is shown in Figure 7 along with the EL spectrum for the single-layered device with polymer **IV**. In both cases peak emission occurs at ~500 nm, which appears light blue to the naked eye. The EL spectrum shows, however, that the emitted light has a substantial green component. In both examples, the emission wavelength and the broadness of the emission peak suggest that pyrene excimer is responsible for light in these devices.[32]

Conclusions

A new polymer containing pendent triarylamine units was synthesized. The new triarylamine polymer has a low oxidation potential and shows great promise as a hole injection material in polymer LEDs. As a hole injection layer the polymer has been used to substantially improve the brightness and quantum efficiency of an LED comprising an electroluminescent polymer with pendent luminescent groups. Typical internal efficiencies of the two-layered devices which incorporated the hole transport polymer **III** and electroluminescent polymer **IV** were 0.20%. The electroluminescent elements emitted blue-green light with a maximum intensity of ~170 cd/m^2. Optimization of the EL polymer−cathode contact should lead to further improvements in the devices brightness and efficiency.

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