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Amorphous Poly-2,7-fluorene Networks

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We have developed a novel strategy for the synthesis of emitters, based on amorphous poly-2,7-fluorene (2,7-PF) networks which exhibit high glass transition temperatures and good photoluminescence properties and are suitable for incorporation into multilayer light-emitting diodes (LEDs). The materials design includes nickel(0)-mediated copolymerization of 2,7-dibromo-9,9-dihexylfluorene with a tetrafunctional spiro-compound, 2,2′,7,7′-tetrabromo-9,9-spirobifluorene, and 4-bromostyrene as end-capping reagent. The introduction of the spiro-bifluorene leads to a 90° branch of the growing 2,7-PF chain, the number of which can be controlled via the feed ratio of monomers used. The termination of the growing network with 4-phenylethenyl end groups limits the molecular weight, hence keeps the material soluble and processable. The oligomer solution can be cast into thin films and thermally cross-linked leading to new amorphous 2,7-PF networks. The amorphous 2,7-PF networks were incorporated in bilayer and trilayer LED devices which emitted colorfast blue light.

Introduction

Since their discovery,[1] electroluminescent organic materials have attracted a good deal of industrial interest driven by the huge market potential of this novel technology.[2] While small molecule-based full-color electroluminescent devices are beginning to appear,[3] conjugated polymer-based displays—highly desirable because of their ease of fabrication and the possibility of building flexible displays—still suffer from the lack of a long-term stable blue emitting material. The shortcomings of these high band-gap polymers—typical poly-*para*-phenylene (PPP) derivatives—arise from their intrinsic structural features: the rigid backbone of these materials leads, via $\pi-\pi$-interaction, to the formation of aggregates and excimers upon thermal treatment or passage of current, resulting in quenching of the highly efficient emission of the single polymer chains that is observed in solution.[4]

Among the PPP derivatives, poly-2,7-fluorene (2,7-PF) containing two planarized benzene rings per monomer unit, is being considered by several research and industrial groups as the most promising blue-light-emitting material due to the chemical and thermal stability, high photoluminescence quantum efficiency, and ease of property tunability through structural modification of the 9-position of the fluorene ring.[5] The ideal high band-gap material for light-emitting diodes (LEDs), however, would be a highly amorphous polymer exhibiting good solubility and having almost no tendency to aggregate in the solid state. Two main concepts have been applied to control and stabilize the amorphous state in solid thin films of conjugated polymers: the first approach involves lowering the crystallization tendency of the rodlike macromolecules by introducing bulky solubilizing groups in the side chain[6] or at the end of the polymer chains,[7] synthesizing copolymers,[8] or introducing saturated spacers in the polymer main chain.[9] A second approach to maintain the amorphous state at elevated temperatures is to introduce spiro-linkages into a molecular structure.[10] The previous studies have shown that solubility can be enhanced, crystallization tendency can be minimized and T_g can be increased by synthesizing a spiro-bifluorene containing a tetrahedral bonding atom at the center of two biphenylene units. This structure maintains a 90° angle between the connected conjugated units via a σ-bonded network and was shown to operate as an emissive layer in organic LED structures. More recently such spiro-structures have shown that both T_g and color stability can be enhanced in alternating 2,7-PF copolymers.[11]

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Another consideration in materials design for polymeric LEDs includes the process compatibility: multilayer polymer diode structures which may consist of two or more distinct organic layers (e.g., hole and electron injection polymers, emitting polymer) may be applied by successive solution spin coating steps. This requires that no material of the underlying layer can be dissolved by the spin-coating process of the next layer. The invention of cross-linkable linear 2,7-PF oligomers[12] and their use in the fabrication of efficient, multilayer LED devices, was a key advance in the preparation of efficient blue polymeric LEDs.[13] One key feature of these materials is their ability to be spun from organic solution, cured to induce solvent resistance and subsequently coated with successive organic solutions, allowing multilayer LED structures to be constructed. In these multiplayer devices the ITO electrodes can be coated with a hole injection material (for 2,7-PF devices usually PEDOT/PSSA)[14] from aqueous solution yielding a thin film that is not soluble in organic solvents from which the subsequent polymers are applied. A promising material used to promote efficient hole-transport are polymeric triphenylamines carrying cross-linkable 4-phenylethenyl end groups.[12b] Thermal treatment of these films render them insoluble in common organic solvents allowing application of the cross-linkable 2,7-PF material.

We wished to combine the advantages of using cross-linkable systems with the structural advantages presented by the use of the spiro-bifluorene unit. Here we present a novel approach toward amorphous 2,7-PF emitters by incorporation of a tetrafunctional spirobifluorene as a three-dimensional building block suitable for incorporation in multilayer LED devices.

Experimental Section

Materials. The Yamamoto coupling reagent bis(1,5-cyclooctadiene)nickel(0) was purchased from Strem and handled under inert atmosphere. The solvents were dried according to standard procedures.[15] All other materials were purchased from Aldrich and used as received. All reactions were carried out under an argon atmosphere.

Instrumentation. The ^{1}H- and ^{13}C NMR-spectra were recorded on a Bruker AF 250 MHz spectrometer. The polymer molecular weights were determined using a Waters gel permeation chromatography (GPC) instrument (Waters PLgel columns: 10^4, 10^3, 500, and 100 Å, Waters 410 Differential refractometer) calibrated with polystyrene standards (Polysciences, Inc.). The optical properties of the polymers **8a−d** were investigated with a Hewlett-Packard 8452A diode array spectrophotometer and a SA Instruments FL3-11 fluorimeter. TGA measurements were performed under a nitrogen atmosphere at a heating rate of 10 °C/min using a Perkin-Elmer TGS-2 instrument. Temperature-modulated differential scanning calorimetry (mDSC) was preformed on a TA Instruments DCS 2920 modulated DSC at a scanning rate of 2 °C/min. Electroluminescence spectra were taken using a spectrograph coupled to a CCD array. Current−voltage and light output−voltage were measured simultanously with a Keithley 238 source measure unit and a calibrated silicon photodiode in an integrating sphere, respectively.

Synthesis of 2,2′,7,7′-Tetrabromo-9,9′-spirobifluorene (5).[10c] A sample of 4.58 g (25.4 mmol) of 9-fluorenone was dissolved in 70 mL of dry diethyl ether, and the mixture was added to a Grignard solution prepared from 625 mg (25.7 mmol) of magnesium turnings, 6 g (25.7 mmol) of 2-bromobiphenyl, and 30 mL of diethyl ether. After the addition was complete, the mixture was refluxed for a further 2 h. After cooling, the yellow precipitate formed was isolated by filtration and hydrolyzed in 100 mL of ice water containing 4 g of ammonium hydroxide. After the solution was stirred for 1 h, the 9-(2-biphenyl)-9-fluorenol formed was filtered off, washed with water, and dried under vacuum. The 9-(2-biphenyl)-9-fluorenol was then dissolved in 55 mL of hot glacial acetic acid, and 0.05 mL of concentrated hydrochloric acid were added. The solution was allowed to boil for 15 min. Then water was added until the solution became turbid. After the solution was cooled, the product was separated by filtration, washed with water, and recrystallized from ethanol to give 1.5 g (4.7 mmol, yield: 19%) of 9,9-spirobifluorene. The 4-fold bromination was conducted by slowly adding a solution of 1.66 g (10.37 mmol) of bromine in 2 mL of methylene chloride to a solution of 0.8 g (2.53 mmol) of 9,9-spirobifluorene and 0.02 g (0.127 mmol) of anhydrous ferric chloride in 10 mL methylene chloride. The resulting mixture was refluxed for 6 h. After the mixture was cooled, the precipitate formed was isolated by filtration to give after drying 0.77 g (1.62 mmol, yield: 64%) of 2,2′,7,7′-tetrabromo-9,9-spirobifluorene (**5**). ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.81 (s, 4 H), 7.51 (dd, $J = 7.91$, 1.80 Hz, 4 H), 7.66 (d, $J = 7.93$ Hz, 4 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 66.2, 121.6, 122.2, 127.3, 132.0, 139.5, 148.8; ^{13}C NMR (125 MHz, $CDCl_3$) δ 45.7 (w), 121.6, 122.2, 127.3, 131.7, 131.8, 139.5, 148.8; UV−vis (THF) $\lambda_{max} = 341$ nm.

General Procedure for the Synthesis of the 2,7-PF Networks 8a−d. A 100 mL Schlenk tube containing 14 mL of degassed toluene, 10 mL of degassed DMF, bis(1,5-cyclooctadiene)nickel(0) (704 mg, 2.56 mmol), 2,2′-bipyridine (400 mg, 2.56 mmol), and 1,5-cyclooctadiene (0.31 mL, 2.56 mmol) was heated under argon to 80 °C for 20 min. The respective reactants (1.22 mmol 2,7-dibromo-9,9-dihexylfluorene, 0.183 mmol 4-bromostyrene, and various amounts of 2,2′,7,7′-tetrabromo-9,9-spirobifluorene) dissolved in 20 mL of degassed toluene were added to the above solution via a syringe, and the polymerization was maintained at 80 °C for 24 h. After the reaction was completed, 50 mL of toluene was added and the solution was filtered over silica. The polymer was precipitated from an 1:1 mixture of methanol and acetone and dried at 60 °C under vacuum. Yield: 63−75%; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.57−0.85 (m, b, 6 H), 0.89−1.34 (b, 16 H), 2.05 (s, b, 4 H), 5.22 (d, $J = 11$ Hz), 5.75 (d, $J = 18$ Hz), 6.72 (dd, 11 Hz, 18.2 Hz), 7.44 (d, $J = 8.3$ Hz, H-3, 6 and H-3′, 6′) 7.52−7.82 (m, 6 H).

LED Device Fabrication and Measurement. Procedures followed for LED device fabrication were similar to those described in ref 12b. Any deviations from those procedures are discussed in detail below in the Results and Discussion section.

Results and Discussion

Our approach is based on utilizing a small amount of a tetrafunctional spiro-bifluorene as a three-dimensional building block and comonomer in the nickel(0)-mediated polymerization of 2,7-dibromo-9,9-dialkylfluorene derivatives in combination with 4-bromostyrene as cross-linkable end-capping reagent. The spiro-bifluorene leads to a 90° branch of the growing 2,7-PF chain (determined by the feed ratio) resulting in a three-dimensional network of 2,7-PF. The termination of the growing network with 4-phenylethenyl end groups plays a key

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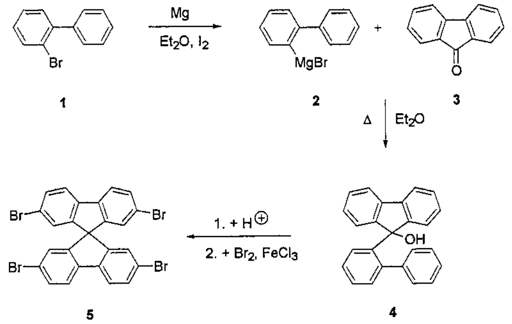
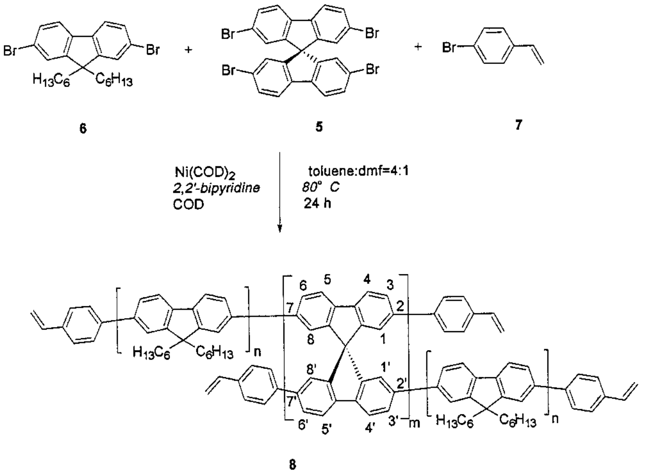
Scheme 1. Synthesis of the Tetrafunctional Spiro-bifluorene 5



Scheme 2. Synthesis of Three-Dimensional Poly-2,7-fluorene Networks 8a−d



role in obtaining a processable material since without the addition of the end-capping reagent the reaction would yield a highly crosslinked, insoluble material. A second purpose of the 4-phenylethenyl termini is to provide reactive functionality that can be thermally triggered to render the material insoluble after spin-coating into a thin film. This offers the ability to utilize this material in multilayer thin film process sequences.

The synthesis of 2,2′,7,7′-tetrabromo-9,9′-spirobifluorene **5** begins by reacting 9-fluorenone with the Grignard reagent of 2-bromobiphenyl followed by acid treatment. The resulting spiro-bifluorene is then brominated in a second step using ferric chloride as catalyst (see Scheme 1). The nickel(0)-mediated Yamamoto polymerization[16] has been used for the copolymerization of the monomers **5**, **6**, and the end-capper **7′** (see Scheme 2). The amount of 4-bromostyrene (**7**) was kept constant in all the polymerization reactions (15 mol % based on 2,7-dibromo-9,9-bishexyl-fluorene). This amount of terminating reagent would afford a linear 2,7-PF with a molecular weight of approximately 7000 g/mol in the polymerization of 2,7-dibromofluorenes.[17] Different amounts of the spiro-cross-linker, ranging from 2 to 20%, were added in order to examine the influence of the monomer:spiro compound ratio on the materials properties (see Table 1). The polymerizations with up to 4% of **5** proceeded smoothly in contrast to the reactions with 10% and 20% spiro-bifluorene, where partial precipitation visible by eye occurred during the polymerization. The resulting polyfluorene networks were isolated and purified by filtration of the reaction mixtures over silica and repeated precipitation steps.

Table 1. Molecular Weight (M_n × 10^3 g/mol), Polydispersity (D), Feed (and Incorporation Ratio (Determined via ^1H NMR), TGA) and DSC Results (Decomposition Temperature T_D at 5% Weight Loss and T_g in °C), and Maximum Concentrations in *p*-Xylene (c_M in mg/mL)

	M_n	D	n:m (feed ratio)	n:m (incorporation ratio)	T_g	T_D	c_M
8a	3.8	3.04	98:2	97.7:2.3	105	435	14
8b	12.8	7.67	96:4	95.7:4.3	144	440	10
8c	4.6	5.25	90:10	98:2	93	430	12
8d	6.4	9.27	80:20	98.1:1.9	90	445	8

The molecular weights were determined using gel permeation chromatography (GPC) and are shown in Table 1. It is well-known, however, that GPC using coillike polystyrene standards tends to overestimate the real molecular weight of linear rigid rod type PPP derivatives.[18] In the case or our three-dimensional materials we note that we cannot rely on GPC as an exact measure of molecular weight. The branched nature of the oligomers are expected to result in deviations from the molecular weights of polystyrene standards and without further study it is difficult to judge if GPC gives an overestimation or underestimation of true molecular weight. Since the oligomers were synthesized to act as chain extendable building blocks, and we confirmed the presence and quantity of both the 4-phenylethenyl end groups and spiro groups by NMR, a measure of the absolute molecular weight of the oligomers was not required: We were able to make use of GPC to give us a relative measurement of molecular weight and more importantly, polydisperisty. The polydispersities of the materials were high as expected and display the random growth of the 2,7-PF networks. The GPC-elution diagrams of **8c** and **8d** are very broad and polymodal which can be ascribed to the partial precipitation of the 2,7-PF network during the reaction. Selective fractionation of a majority of the higher molecular weight material results in a deceptively broad GPC elution profile. The incorporation ratio of the spiro-bifluorene could be analyzed by comparison of the ^1H NMR signal intensities of protons H-3, H-6, H-3′, and H-6′ ($\delta = 7.44$) of the three-dimensional spiro-bifluorene building block with that of the fluorene repeat unit ($\delta = 7.52-7.82$). The considerably lower incorporation than feed-ratio of the soluble fractions of **8c** and **8d** (see Table 1) is probably due to the partial precipitation (visible by eye for **8d**) of the growing 2,7-PF network during polymerization. The thermal properties of **8a**−**d** were investigated using thermogravimetric analysis (TGA) and differential scanning calorimetry (mDSC) and are summarized in Table 1. The 2,7-PF network **8a** already has a higher glass transition temperature (T_g = 105 °C) than poly-2−7-(9,9-dihexylfluorene) (T_g = 75 °C). For comparison, cross-linked linear PFs have been shown to have T_gs ranging from 70 to 105 °C.[12a] It is evident, that an increasing incorporation ratio of the spiro-bifluorene **5**

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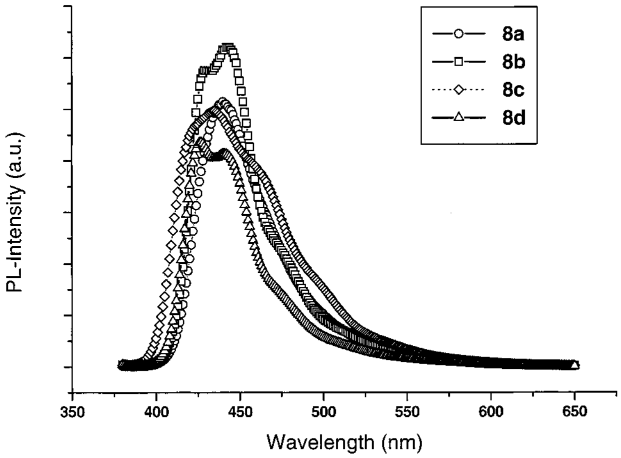

Figure 1. Thin film PL-spectra of **8a**–**d** ($\lambda_{exc.} = \lambda_{max}$).

Table 2. UV- and PL(λ_{exc}=λ_{max})-Data of 8a–d in Solution and Thin Film

	(THF)		(film)	
	λ_{max} [nm]	λ_{em} [nm]	λ_{max} [nm]	λ_{em} [nm]
8a	374	413, 436	375	440
8b	376	414, 438	381	429, 444
8c	375	415, 439	378	435
8d	377	414, 436	381	427, 440

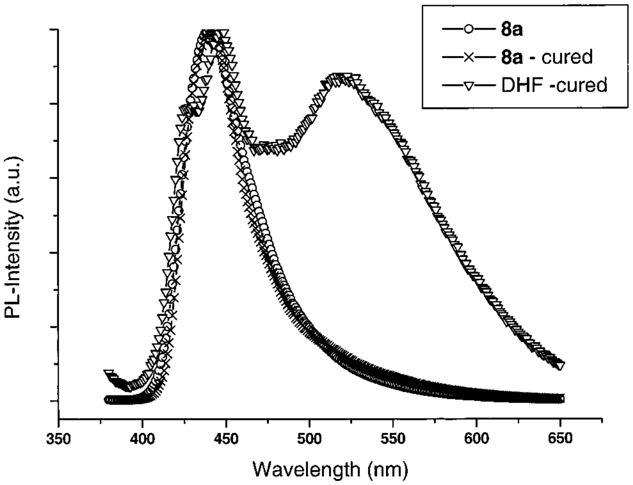

Figure 2. PL-spectra of the uncured and cured amorphous 2,7-PF **8a** and a cured poly-2,7-(9,9-dihexylfluorene).

leads to a higher T_g of the resulting 2,7-PF network. All materials exhibit excellent thermal stability (5% weight-loss above 400 °C), similar to their rigid rod analogues. mDSC measurements showed no evidence of a liquid-crystalline state as observed in other linear 2,7-PFs carrying alkyl chains as solubilizers.[19]

The amorphous 2,7-PFs are soluble in common organic solvents, such as toluene, THF, and *p*-xylene, and exhibit deep blue fluorescence both in solution and thin films. Maximum concentrations in THF range from 8 to 14 mg/mL (see Table 1). According to published UV- and PL-data on monodisperse oligo-fluorenes[20] the emissive properties of the networks **8a**–**d** in solution (THF) result from approximately 5–6 conjugated fluorene units (see Table 2). The data indicate that the statistical incorporation of the spiro-bifluorene **5** into the polymer main chain does not change the electronic nature of the polymer backbone.

Thin films of the amorphous 2,7-PFs **8a**–**d** were prepared by spin-coating on quartz substrates from *p*-xylene solution (c = 10 mg/mL except for **8d** with c = 8 mg/mL) for 60 s at 2500 rpm and dried under high-vacuum for 1 h. The absorption maxima of **8a**–**d** in solid state are slightly bathocromically shifted compared to the solution values due to the decreased torsion angle and therefore increased conjugation of the fluorene repeat units. The fluorescence spectra of the 2,7-PFs **8a**–**d** in thin films are shown in Figure 1. The networks **8a** and **8b** exhibit a weaker vibronic fine structure compared to the derivatives **8c** and **8d**. This observation is probably due to the partial precipitation of **8c** and **8d** during polymerization leading to a block nature in these networks with spiro-bifluorene-rich and spiro-bifluorene-poor blocks. To investigate the optical properties after thermal treatment, the films were heated (hot plate) at 120 °C for 30 min; a process which leads to cross-linking of the 4-phenylethenyl end groups rendering the films insoluble. We chose the thermal conditions based on the onset of the 4-phenylethenyl end group cross-linking exotherm as observed by modulated DSC. Detailed studies of the thermal cross-linking chemistry of similar 4-phenylethenyl-terminated oligomers can be found elsewhere.[12a,21]

Color and luminescence stability under elevated temperatures are very important LED material specifications since real-time IR measurements of working organic LEDs reveal that the temperature inside the devices can exceed 86 °C depending on the operation conditions.[22] It is evident that the applied curing conditions did not cause any spectral change in the emission spectra of **8a**, while the PL-spectrum of the poly-2,7-(9,9-dihexylfluorene) exhibits the appearance of the broad excimer band at ~540 nm leading to blue-green emission.

A solution of the 2,7-PF network **8b** in *p*-xylene (c = 7.5 mg/mL) was selected to build multilayer (bi-layer and three-layer) LED devices due to the excellent film-forming and spinning characteristics of **8b** leading to high optical quality films. The bilayer device was fabricated in an indium tin oxide (ITO)/polyethylenedioxythiophene-polystyrenesulfonate (PEDOT-PSSA, Bayer Baytron-P)/cross-linkable poly(4-*n*-hexyl-triphenyl)amine (x-HTPA)/**8b**/Ca/Al configuration. After spin-coating of the hole-transport layer x-HTPA (thickness: 70 nm) the device was cured for 1 h at 100 °C in a glovebox, a process which was repeated after spin-coating of **8b** (thickness: 75 nm) to cross-link the 4-phenylethenyl termini. The diode started to emit deep blue light at 3 V with an emission maximum at 424 nm (CIE coordinates C_x, 0.168; C_y, 0.07). The EL-spectrum displays no sign of aggregate or excimer formation and is shown in Figure 3. The maximum external quantum efficiency of the diode was determined to be 0.08% at 9 V. Despite the low external EL-QE of **8b**, the bilayer device showed good color stability, as seen by the lack

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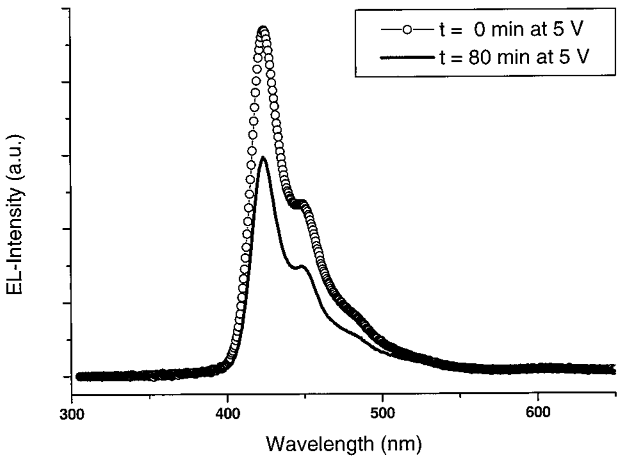

Figure 3. EL-spectrum of 2,7-PF 8b (dotted line: starting El-Intensity/straight line: El-Intensity after 80 min).

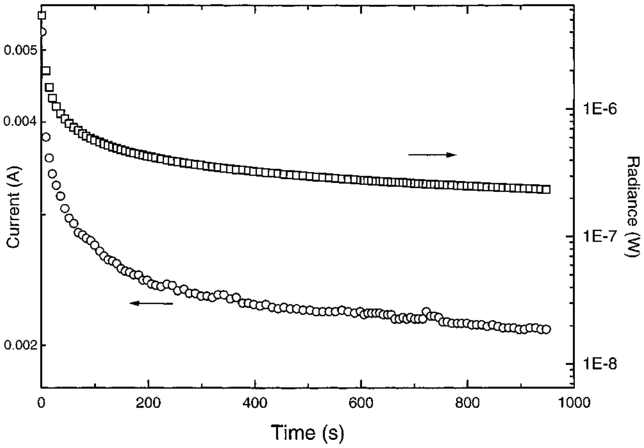

Figure 4. Luminescence and current stability data as a function of continuous operation for a two layer device of 2,7-PF **8b**. ITO/PEDOT-PSSA/x-HTPA (70 nm)/**8b** (75 nm)/PPQ-F6 (25 nm)/Ca/Al.

of any noticeable color shift after operation (see Figure 3). To investigate whether using a poly-phenylquinoline derivative (PPQ-F6)[23] as an electron-transport layer improves the EL-performance of the 2,7-PF network **8b**, LEDs were manufactured in an ITO/PEDOT-PSSA/x-HTPA (70 nm)/**8b** (75 nm)/PPQ-F6 (25 nm)/Ca/Al. The three-layer device, however, did not show superior EL performance compared to the bilayer device but exhibited similar diode characteristics (turn-on voltage, 4 V; EL emission maximum, 423 nm; CIE coordinates C_x, 0.173; C_y, 0.098; external EL-QE, 0.06%).

When the devices were initially turned on they go through a one-time burn-in stage exhibiting a fast initial drop in output intensity. This one-time decline is commonly seen in polymeric LEDs and the cause is not known, but probably has to do with migration of ionic impurities and electrochemical changes at the electrode interfaces. Upon continuous operation, the devices emit fairly stable blue light with a slow stretched exponential decay in output intensity over time. A typical current/radiance vs time plot is shown in Figure 4. While no long-term stability testing has been done with these materials, the plateau in the decay profile allows us to state that these devices possess good stability when compared to other PF-based blue LED devices. Long-lifetime device operation is key to successful use of polymeric materials in practical LED devices and work is underway to better understand device stability issues. We offer our information on the stability of our materials, but clearly more needs to be done in this area and unfortunately very little information concerning the lifetime of blue polymer-based devices can be found openly in the literature.

Conclusions

In conclusion we have presented a novel approach toward amorphous polymeric emitters suitable for multilayer LED fabrication by incorporating small amounts of a three-dimensional spiro-bifluorene building block into the backbone of poly-2,7-fluorene and using bromostyrene as chain terminating reagent. The materials exhibit high glass-transition temperatures and excellent thermal stability and are soluble in common organic solvents allowing for multilayer devices to be fabricated after thermal cross-linking of the cast films. Film−PL-measurements after thermal treatment reveal that these amorphous 2,7-PFs emit color-stable blue light without aggregate or excimer formation. The two- and three-layer LEDs emit blue light at low turn-on voltages and possess good color stability and only a slow luminescent decay during continuous operation. Future work concentrates on improving the EL-efficiency by optimizing device structures in respect to hole- and electron-injection materials and varying the molecular weight of the amorphous 2,7-PFs.

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[23] Bacilieri, C.; Lee, V. Y.; Miller, R. D. Unpublished results.