

Cross-linkable Polymers Based on Dialkylfluorenes

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We have prepared a series of cross-linkable oligo- and poly(dialkylfluorene)s by nickel(0)-mediated polymerization of 2,7-dibromo-9,9-dialkylfluorene (alkyl = *n*-hexyl) and 4-bromostyrene. The resulting fully soluble and processable, styryl-functionalized oligomers and polymers can be cross-linked via the vinyl end-groups by curing at 175–200 °C, consistent with the autopolymerization mechanism of styrene. These relatively mild conditions render the materials insoluble and enable multilayering of polymers in organic light emitting devices. At the same time, the electrical and/or optical properties of the cross-linked polymers are preserved and no deleterious species or undesirable byproducts are produced. Furthermore, the cross-linking allows control of the supramolecular ordering of the planarized rigid rod-type fluorene segments in the polymer backbone that leads to suppression of troublesome excimer/aggregate in the photo- and electroluminescence.

Introduction

Small molecules, oligomers, and polymeric materials constitute active components of organic light-emitting diodes (OLEDs).^{1–4} The simple purification and characterization of small molecules and oligomers as well as their facile incorporation into multilayer devices by vacuum deposition techniques has stimulated research in this field.

Some potential advantages of polymers over small molecules include the possibility of extended π -conjugation, generally higher glass transition temperatures, excellent film-forming properties, stable film morphologies, and simplified processing via spin-coating.¹ One drawback of processable polymers is the frequent inability to spin-cast multiple layers to independently control device operating parameters such as emission, charge injection, and/or transport. Casting of polymer multilayers is often complicated because the lower layers are usually soluble in the solvents used for casting succeeding layers. In rare cases (for example, poly-*p*-phenylenevinylene), there is a suitably soluble precursor polymer which becomes insoluble on conversion to the desired electroactive form. However, the conversion process frequently involves extreme processing conditions and reactive byproducts which can influence the performance of the finished device. Very recently, reports of cross-linkable polymeric hole transport and/or electroluminescent materials to facilitate the construction of solution processed multilayer devices have appeared.⁵

Poly(alkylfluorene)s are promising materials for OLED applications because of their high photoluminescence yields and thermal and oxidative stability.⁶ We have recently studied poly(di-*n*-hexylfluorene) and various copolymers which upon annealing or the passage of current in polymer films develop additional broad, red-shifted emission bands in the region of 500–600 nm.⁷ Unanticipated red shifts in the emission spectra of planarized π -systems have been variously attributed to the formation of excimers and/or aggregates.⁸ The former involve interchain interactions in the excited state while the latter are associated with ground-state interactions. Emissive excimers and exciplexes have been reported for a variety of π -conjugated polymers.⁹ Likewise, aggregates have been reported in a variety of conjugated polymers.¹⁰ The presence of film aggregates is often detected in absorption as well as by fluorescence excitation and site selective fluorescence. In the case of poly(di-*n*-octylfluorene), evidence for both

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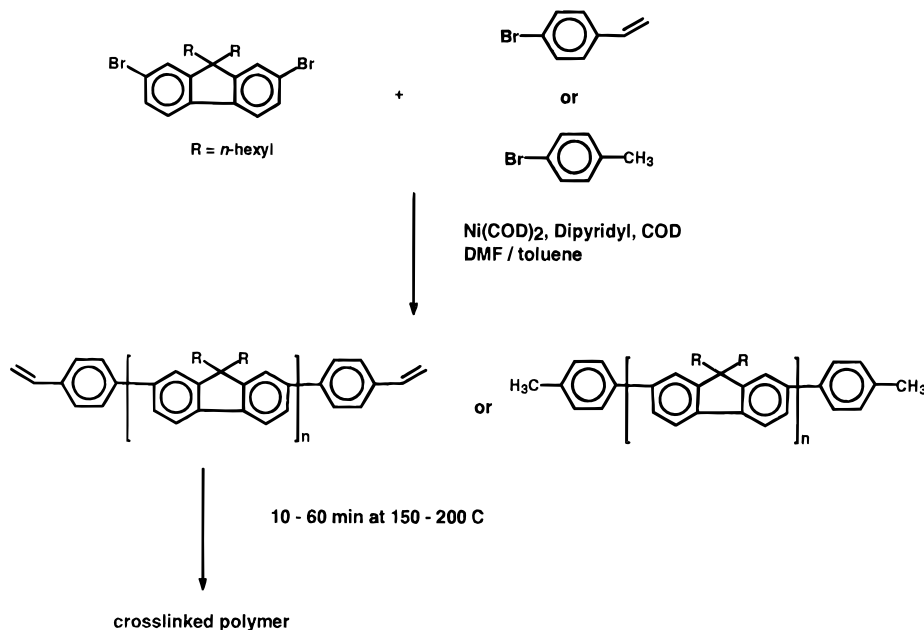
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Scheme 1. Yamamoto-Type Polymerization of 2,7-Dibromo-9,9-di-*n*-hexylfluorene in the Presence of Either 4-Bromostyrene or 4-Bromotoluene (Cross-linking and Non-cross-linking End-Caps, Respectively)



aggregates and emissive excimers has recently been reported.¹¹ Here the aggregate emission is vibronically structured and significantly blue-shifted from the broad, featureless excimer emission. The relative importance of each to the film emission properties depends on polymer structure and the film morphology. Previously we also have reported a broad, structureless emission from a variety of polyfluorene copolymer films.⁷ Here, we assume that the broad, red-shifted emission produced upon thermal annealing of films of poly(di-*n*-hexylfluorene) is primarily due to excimer formation rather than aggregates.

We have also recently reported polymer end-capping techniques using 2-bromofluorene which remove bromine end-groups that could quench the emission and lead to stability problems in LED applications. End-capping also enables molecular weight control, and we have described the preparation of a homologous series of oligo(di-*n*-hexylfluorene)s, from which the effective conjugation length for absorption was estimated as ~12 fluorene units.^{12,13}

We now report that end-capping procedures can be used to not only control molecular weights but also for the introduction of reactive functionality at the chain

ends. The proper choice of the functionality within the polymer chain allows control of polymer properties such as emission color and processibility.

Results and Discussion

Different molecular weight homopolymers derived from 2,7-dibromo-9,9-di-*n*-hexylfluorene were prepared using zerovalent nickel (Scheme 1)¹⁴ and end-capping with 4-bromostyrene. Molecular weight control in the end-capped polymers was achieved by altering the ratio of bifunctional to monofunctional monomers. The comonomer ratios in this study were typically either 2:1 or 6:1 (Table 1).

When 4-bromostyrene was present from the polymerization onset, 33 mol % of end-capper led to a 9,9-di-*n*-hexylfluorene homopolymer (PDHF) with a number average molecular weight (M_n) of 3 500 (determined by gel permeation chromatography). Less monofunctional end-capper (e.g., 15 mol %) led to higher molecular weights ($M_n = 19 000$). To study the effect of polymer cross-linking on the overall polymer properties, we also prepared non-cross-linkable poly(di-*n*-hexylfluorene)s with similar molecular weights using 4-bromotoluene as an end-capper. The molecular weights were determined by gel permeation chromatography (GPC) using polystyrene standards. The GPC traces of the low molecular weight samples showed the presence of some oligomer as well as low molecular weight polymers.

The styryl-functionalized DHF homopolymers are initially soluble in common organic solvents such as THF, chloroform, xylene, chlorobenzene, etc. A representative ¹H NMR spectrum of PDHF end-capped with styrene is shown in Figure 1. The vinyl protons of the end-caps are clearly visible in the region δ 5.0–7.0. For each of the copolymer examples studied (PDHF/DSF,

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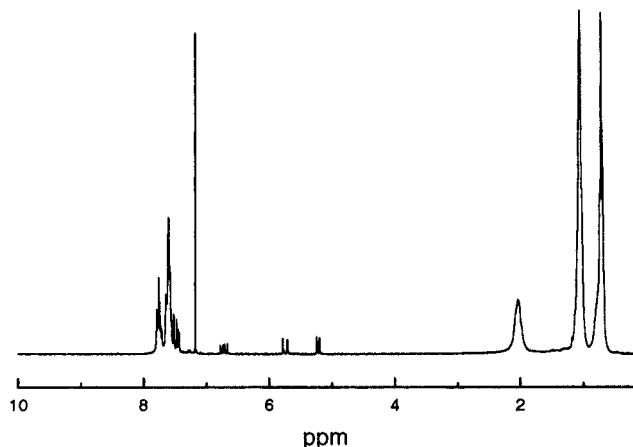
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Table 1. Polymer and Optical Properties of End-Capped Poly(di-*n*-hexylfluorene)s

copolymer	$M_n (\times 10^3)^a$	PDI	no. of repeat units		wt % styryl funct ^b	T_g (°C)	λ_{\max} (nm) ^c	
			<i>a</i>	<i>b</i>			absorption	emission
DHF 85/4-Br-styrene 15	19	1.9	63	34	2	101	382	425/450
DHF 67/4-Br-styrene 33	3.5	2.8	12	11	6	80	374	423/447
DHF 85/4-Br-toluene 15	17.7	1.9	59	36	-	95	380	426/451
DHF 67/4-Br-toluene 33	2.9	1.7	12	7	-	70	375	425/450
DHF 85/DSF (distyrylfluorene) 7.5/ 4-Br-toluene 7.5	19.4	2.0	64	42	4	105	385	425/450
DHF 60/DSF 7.5/4-Br-toluene 32.5	3.4	1.8	12	7	6	78	376	424/449

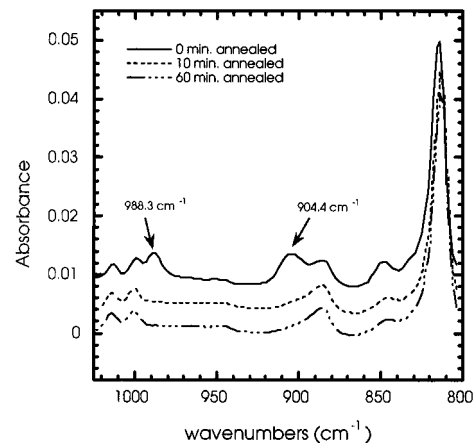
^a Measured by gel permeation chromatography (GPC) referenced to polystyrene standards. ^b Measured by ¹H NMR integration of end-groups vs C-9- α -methylene protons of di-*n*-hexylfluorene. ^c Measured in thin films on quartz wafers.

**Figure 1.** ¹H NMR of PDHF ($M_n = 3500$) end-capped with 4-bromostyrene.

vide infra), the composition of the statistical, random copolymers tracks the monomer feed ratio. This analysis was performed by ¹H NMR integration of the C-9 α -methylene signals from the di-*n*-hexylfluorene unit ($\delta = 1.8$ – 2.4) relative to the total of the aromatic signals. End-group analysis of the lower molecular weight PDHF/STYR materials by ¹H NMR (integration of the C-9 α -methylene signals from the dialkylfluorene main chain unit relative to the signals from the vinyl protons of the styryl end-groups) provides a value for M_n to be compared with that determined by GPC analysis (Table 1). The latter value, which is referenced to polystyrene standards, is always somewhat greater than that determined by ¹H NMR. This difference is not surprising given the rodlike nature of PDHF relative to the random coil polystyrene standard. On the basis of the degree of polymerization and by assuming two styryl groups/chain,¹² the weight % styrene/polymer chain in each sample is calculated. Similarly, the weight % of styryl units/polymer chain in the PDHF/DSF random copolymers can be determined (Table 1).

The polymers are thermally stable (5% weight loss values above 400 °C for all samples as measured by thermal gravimetric analysis (TGA) (10 °C/min)) and have initial glass transition temperatures ranging from 70 to 105 °C (determined by modulated differential scanning calorimetry (MDSC) analysis (4 °C/min)).

To study the cross-linking process, we have monitored the reaction by IR, MDSC, and thin-film insolubilization. The latter could be determined by recording the absorbance at λ_{\max} as a function of heating time before and after rinsing with chloroform. The un-cross-linked films were completely removed upon rinsing. The cross-linking was performed in an inert atmosphere as the

**Figure 2.** In situ IR study of the cross-linking reaction of PDHF ($M_n = 3500$) annealed at 200 °C in nitrogen.

presence of oxygen during curing led to the appearance of a carbonyl absorption in the IR at 1722 cm^{-1} . IR spectra of thin films of the cross-linkable PDHF samples display weak bands characteristic of the styryl units prior to cross-linking (Figure 2). Peaks around 905 and 990 cm^{-1} correspond to the vinyl C–H out-of-plane bending vibrations. A terminal vinyl C=C stretching absorption is also observed in the IR at around 1630 cm^{-1} before heating. After the film was annealed for 10 min, all three of these characteristic vinyl peaks decreased significantly (Figure 2) and the films became insoluble. Weaker bands around 1165 to 1175 cm^{-1} , which appeared after heating, were attributed to new C–C stretching vibrations. The disappearance of the characteristic vinyl peaks and the appearance of new carbon–carbon single bonds suggests that the cross-linking of the styryl end-groups is largely completed after only 10 min heating for the low molecular weight bis-styryl end-capped PDHF. UV–visible studies of these films which had been heated for 10 min and then washed with chloroform showed essentially no change in the absorbance values at λ_{\max} after rinsing.

The continuous measurement of sample heat flow and heat capacity by temperature-modulated DSC often allows the monitoring of the reactions of thermosets.¹⁵ Figure 3 shows the first, second, and third heatings of the low molecular weight cross-linkable PDHF terminated with styryl units ($M_n = 3500$, GPC). The reversible heat capacity for the first heating reveals a T_g at around 80 °C and an exothermic transition near 175 °C. The second and third heatings display significantly higher T_g s at 125 and 130 °C, respectively, and the

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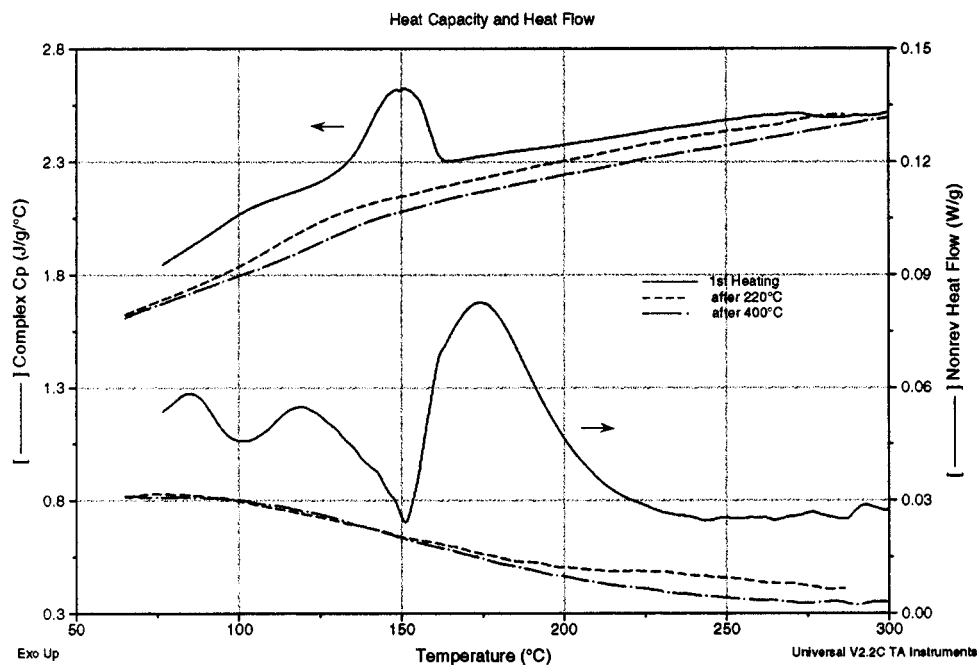


Figure 3. Modulated DSC study of the cross-linking reaction of PDHF ($M_n = 3500$) terminated with styryl units.

transition around 175 °C is no longer detectable. This suggests that thermal cross-linking reactions produce an amorphous rigid polymer network. In addition, the nonreversible heat flow observed during the initial but not subsequent heatings detects the cross-linking reaction by the appearance of an exotherm at 150–200 °C associated with the consumption of the reactive functionality.

The spectroscopic properties of the poly(di-*n*-hexylfluorenes) were measured on thin films (100–150 nm). The absorption spectra all show a broad, featureless absorption with λ_{max} ranging from 375 to 385 nm for the DHF homopolymers. The low molecular weight styryl-terminated material displayed a small blue shift (4–8 nm) in the absorption maximum upon thermal annealing which may be attributed to the consumption of the vinyl unit in the 4-position of the end-cap which is conjugated with the polymer backbone.

After annealing at 200 °C for 12 h, the non-cross-linkable PDHF samples display a bathochromically shifted emission around 520 nm in the photoluminescence spectra in addition to the intrinsic structured blue emission at 425 nm, characteristic of the isolated chains (Figure 4a). We attribute the former to excimer formation due to polymer chain π -stacking.

The annealing experiments with the corresponding terminal styryl functionalized PDHF samples reveal a distinctly different behavior from the non-cross-linkable systems. In this case, thermal curing at 200 °C for up to 12 h does not produce any significant changes in the PL emission spectra (Figure 4a). During this period, thermal cross-linking via the reactive functionality is certainly essentially complete. Although it has been reported that films of poly(dialkylfluorenes) terminated with benzocyclobutene substituents also cross-link upon curing to higher temperatures (250 °C), the emission of these cured films is dominated by a longwave emission in the region 530–550 nm which is attributed to excimers and/or aggregates.^{5c} The cross-linking of the styryl functional chain ends thus leads to complete

suppression of the morphology changes which lead to the longer wavelength emissions in the non-cross-linkable samples. This result is rationalized by the assumption that cross-linking via the end-groups greatly inhibits chain mobility and hence the ability of the planar rigid rod chains to orient intermolecularly in a coplanar fashion in order to π -stack.

Significantly, a similar trend is observed in the electroluminescence (single layer, ITO/PDHF/Ca) (Figure 4b). In the case of the non-cross-linkable PDHF, both the annealed PL and the unannealed EL spectra are complicated by long wavelength emissions. For the EL spectra reported in Figure 4b, a higher molecular weight non-cross-linking PDHF sample ($M_n = 15\,000$) was used to improve the film quality. As we have recently reported that the rate of excimer/aggregate formation upon annealing strongly depends on the sample molecular weight (i.e., lower molecular weights result in more excimer/aggregate emission),¹⁶ the differences in the EL spectra shown in Figure 4b are even more dramatic. Furthermore, long wavelength emissions in un-cross-linked PDHF samples are always exacerbated in EL relative to PL. This is manifested by a rapid change in the EL emission color from blue to white during device operation. The electroluminescence spectrum of the low molecular weight ($M_n = 3\,500$) sample of PDHF terminated with styryl units which had been thermally cross-linked during the device fabrication, on the other hand, showed little of the long wavelength emitting species, suggesting that immobilization of the polymer chains leads to suppression of intermolecular excited state interactions (Figure 4b). When the cross-linking functionality is introduced through the end-caps, the effective concentration of reactive functional groups depends on the polymer molecular weight. The lower the polymer molecular weight, the higher the chain mobility and the more

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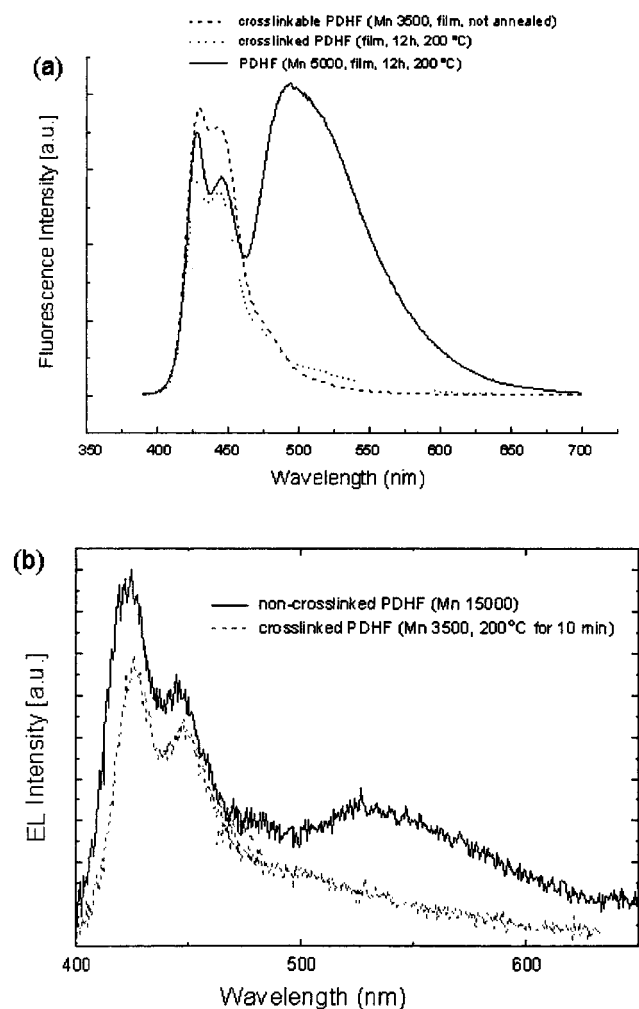
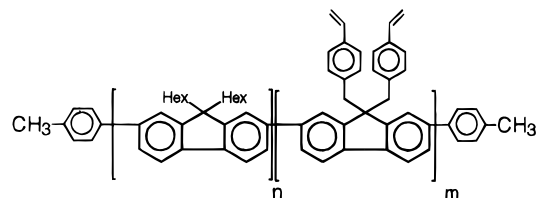


Figure 4. PL and EL spectra of cross-linking and non-cross-linking PDHF before and after annealing: (a) photoluminescence and (b) electroluminescence. Device configuration: Ca/PDHF/ITO.

reactive end-groups available for the cross-linking reaction. The latter may be quantified by the calculated weight % styryl functionality/polymer chain listed in Table 1. For the cross-linking samples studied here, the intrinsic tendency of lower molecular weight oligomers to more easily associate is apparently compensated by the increasing cross-linking density. Preliminary results suggest that the suppression of excimer formation in higher molecular weight samples ($M_n > 30K$) which contain fewer cross-linkable groups is somewhat less efficient, an effect which presumably results from the lower concentration of reactive functionality. As a result, we find that the most efficient suppression of π -stacking through cross-linking occurs for initial polymer M_n values ranging from 3 000 to 5 000 (GPC analysis).

To investigate the general applicability of polymer cross-linking for other polymer architectures (e.g., multi-block copolymers), we have incorporated similar cross-linkable functionalities randomly into the DHF polymer backbone but not at the polymer ends. Here, a 2,7-dibromofluorene derivative with two *p*-benzylstyryl groups in the 9-position (prepared by alkylation of 2,7-dibromofluorene with 4-bromomethylstyrene using NaH in THF) can be copolymerized with 2,7-dibromo-9,9-di-*n*-hexylfluorene and end-capped with 4-bromotoluene to yield copolymers (PDHF/DSF) with similar molecular

Scheme 2. Copolymer (DHF/DSF) Containing Internal Cross-linking Sites in the 9,9-Position of Some of the Fluorene Units



weights and weight % styryl groups/chain as the corresponding terminal functionalized materials (Table 1). Studies reveal that the films with reactive functionality present either as end-caps or as main chain grafts are rendered insoluble upon heating to 200 °C in 10–60 min depending on the polymer molecular weight. However, the investigation of the respective PL spectra shows that the internal cross-linking (Scheme 2) does not lead to complete suppression of longer wavelength emissions. This is reasonable given the importance of the nature of the end-groups and chain mobility to this process. Reaction at the chain termini drastically decreases the mobility of the chain ends and hampers the intermolecular chain–chain interactions while reaction through internal chain substituents apparently does so less efficiently. While internal cross-linking is less effective at providing emission color stability in the PDHF/DSF copolymers, it still provides a potentially useful route to insolubilize more complex polymer architectures such as polyfluorene ABA block copolymers for OLED applications.¹⁷

In summary, the synthesis of a series of soluble, easily processable di-*n*-hexylfluorene homopolymers end-capped with 4-bromostyrene with controlled molecular weights can be achieved by the nickel-mediated coupling reaction. The subsequent thermal cross-linking reaction was monitored by IR studies and by modulated DSC. Short-term thermal annealing at 175–200 °C rendered the materials insoluble in common organic solvents which enables multilayering of organic polymers in light-emitting devices using spin-casting techniques. The cross-linking via the polymer chain ends effectively immobilizes the polymer chains and hampers their ability to π -stack, an effect which leads to suppression of the red-shifted emission attributed to excimer formation and enables the fabrication of color-fast blue-light-emitting devices.

Experimental Section

Instrumentation. Thermogravimetric analysis (TGA) and different scanning calorimetry (DSC) of the polymers were performed under a nitrogen atmosphere at a heating rate of 10 °C/min using Perkin-Elmer TGS-2 and DuPont 2100 instruments, respectively. Polymer molecular weights were determined using a Waters 150-C gel permeation chromatography instrument calibrated with polystyrene standards. The synthesized compounds were identified by their ¹H and ¹³C NMR spectra which were obtained using a Bruker AF250 NMR spectrometer. To investigate the photoluminescence properties, the polymers were spin-coated on fused quartz wafers and absorption and emission spectra of the polymer

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films were measured using a Hewlett-Packard 8452A diode array spectrophotometer and SA instruments FL3-11 fluorimeter, respectively. FT-IR spectra were recorded on a Nicolet Magna IR 550 spectrometer.

4-Bromotoluene, 2,7-dibromofluorene, 4-bromostyrene, dipyridyl, 1,5-cyclooctadiene, and bis(1,5-cyclooctadiene)nickel(0) were purchased from Aldrich Chemical Co. and were used as received. The *N,N*-dimethylformamide solvent was distilled from calcium hydride and stored under N₂ until use. The monomer, 2,7-dibromo-9,9-di-*n*-hexylfluorene was prepared by reaction of 2,7-dibromofluorene with *n*-hexyl bromide in the presence of base according to a literature procedure.¹⁸

2,7-Dibromo-9,9-bis(4-vinylphenyl)methylfluorene (DSFBr2). Ten grams (62 mmol) of 2,7-dibromofluorene and 22.9 g (150 mmol) of *p*-chloromethylstyrene were dissolved in 100 mL of toluene and 50 mL of NaOH (50 wt % in water) was added to the above solution. Tetra(*n*-butylammonium bromide) (0.1 g) was added to the above mixture as a phase-transfer catalyst. The color of mixture turned dark brown as soon as phase-transfer catalyst was added. The mixture was stirred at room temperature for 12 h. Ethyl acetate was added and the organic phase washed with water several times. The organic layer was dried over anhydrous magnesium sulfate, and the solvent was removed by rotary evaporator. The product was obtained by precipitating in *n*-hexane and methanol. The yield was 28 g (81%): ¹H NMR (CDCl₃) δ 7.5–7.0 (m, 6H), 6.9 (d, 4H), 6.5 (d, 4H), 6.5–6.3 (q, 2H) 5.5 (d, 2H), 5.0 (d, 2H), 3.2 (s, 4H); ¹³C NMR (CDCl₃), δ 150.1, 138.9, 136.5, 135.8, 135.5, 130.5, 130.3, 127.8, 125.3, 121.3, 120.6, 113.2, 57.2, 45.0.

Polymerization. Homopolymers and statistical copolymers were synthesized by nickel(0)-mediated polymerization. A Schlenk tube containing 6 mL of toluene, 6 mL of DMF, bis(1,5-cyclooctadiene)nickel(0), 2,2'-dipyridyl, and 1,5-cyclooctadiene (the latter three in molar ratios (1:1:1)) was heated under N₂ to 80 °C for 0.5 h. 2,7-Dibromo-9,9-di-*n*-hexyl fluorene (0.5 mmol) in 4 mL of degassed toluene (molar ratio of monomers

and end-capper/nickel complex = 0.57) was added to the above solution and the polymerization maintained at 80 °C for 24 h. After reaction, the polymer was precipitated from an equivalent mixture of concentrated HCl, methanol, and acetone. The isolated polymer (346 mg, 80%) was dissolved in chloroform and reprecipitated into methanol. The solid was dried at 60 °C under vacuum: ¹H NMR (CDCl₃) δ 7.3–7.9 (ring aromatic protons), 1.9 (br s -CH₂C₅H₁₁), 1.0 (m -CH₂(CH₂)₅-CH₃), 0.6 (m, (CH₂)₅CH₃), 6.7, 5.75, 5.20 (vinyl protons of end-caps); *M*_n = 3500; PDI = 2.8; *T*_g ~ 80 °C (DSC); UV (film) = 374 nm.

The other polymers described in Table 1 were prepared in a similar manner by adjusting the stoichiometries of the monomers and end-capping reagents.

Single-Layer LED Fabrication and Measurements. Single-layer LED devices were fabricated using poly(di-*n*-hexylfluorene) end-capped with 4-styrenyl substituents (*M*_n = 3500, PDI = 2.6). The polymer was spin-coated onto a patterned ITO/glass substrate at 1500 rpm from cyclohexanone solution (30 mg/mL). Curing was done at 200 °C for 15 min in a nitrogen atmosphere to form an insoluble layer 80 nm thick. Calcium (Ca) cathodes 25 nm thick were then deposited in a deposition chamber, pumped to a pressure of 10⁻⁶ Torr, through a shadow mask defining six individually accessible devices (each 3.1 mm²). Finally, with the use of the same mask, a layer of Al (25 nm) was deposited to provide additional protection for the reactive Ca.

Electroluminescence (EL) spectra were taken using a spectrograph coupled to a CCD array. Current–voltage and light output voltage were simultaneously measured with a Keithley 238 Source Measure Unit and a calibrated silicon photodiode

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