Novel Stable Blue-Light-Emitting Oligofluorene Networks Immobilized by Boronic Acid Anhydride Linkages

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Thermal dehydration of boronic acid groups to form six-membered boronic acid anhydride (boroxine) was employed as a means of immobilizing oligofluorenes. This approach appears to improve the photoluminescenct stability of the cross-linked films compared to polyfluorenes. The emergence of long-wavelength emission upon thermal treatment usually observed in polyfluorenes has been prevented in this system. Initially the fluorene dimer (**F2BA**), trimer (**F3BA**), and tetramer (**F4BA**) containing boronic acid groups were prepared. These compounds were found to be readily soluble in common solvents such as THF, acetone, and DMF. Transparent thin films of these materials could be easily prepared by casting their solutions in THF onto KBr disks or glass substrates. Using mild reaction conditions (60−130 °C under vacuum for 2 h), these oligomers in the solid sate readily undergo cross-linking reactions by the dehydration of boronic acid groups as evidenced by FT-IR spectroscopy and DSC/TGA studies. The resulting cross-linked amorphous networks exhibit high thermal (T_d at 5% weight loss, 363−420 °C) and morphological (T_g, 173−202 °C) stability. Under UV irradiation, these compounds emit bright violet-blue (**F2BA**) and blue (**F3BA** and **F4BA**) light both in solution and in the solid state. The cured films exhibited almost identical UV−vis and fluorescence spectra even after heating at 150 °C for 24 h, showing no long wavelength emission. The fabrication of LED devices using **F3BA** or **F4BA** as the light-emitting layer and a carbazole diboronic acid (**CzBA**) as the hole-transporting layer demonstrated that these thermally curable diboronic acids can be used to achieve double- (or multi-) layered configurations.

Introduction

Conjugated polymers serving as emitters in light-emitting diodes (LEDs) are attractive to the display industry because of their potential for easy and cost-effective processing by solution casting. In addition they have excellent mechanical properties that allow for the fabrication of flexible and large area displays. At the same time, by structural control, it is possible to tune the electro- and photophysical properties.[1] Among the conjugated polymers considered for LED applications, polyfluorene derivatives have been viewed as the most promising blue light emitters due to their high photoluminescence efficiency, and excellent chemical and thermal stabilities.[2] However, the relatively poor optical stability of these polymers has been a major concern. For example, these polymers often show long wavelength emissions in the region of 500−600 nm accompanied by a drastic reduction in emission efficiency upon heating or passage of current.[3] Although the causes underlying these phenomena are still the subject of intensive investigation, fluorenone formation by the chain oxidation[4] and chain aggregation facilitated by interchain $\pi-\pi$ interaction[5] are generally believed to be

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responsible. Stable blue emitting has been achieved by doping polyfluorene with hole-transporting materials to balance the charge transport or by inserting a buffer layer between the polyfluorene layer and the Ca/Ag electrode.[6] These modifications in the devices avoid high charge density in the polymer layer and prevent the immigration of calcium ion into the polymer layer and thus reduce the oxidation tendency of the polymers during operation. Several other attempts have also been made to minimize the aggregation by chemical modification, including incorporation of bulky substituents at the 9-position of fluorene as a means of increasing the distance between polyfluorene backbones,[7] copolymerization with other monomers for introducing kinks into the polymer chain, which hampers the chain alignment,[3e,8] and thermal cross-linking of fluorene oligomers via styryl end groups.[9] The chain movement in this case was hindered by the presence of cross-linking units. The reduction of the tendency for chain aggregation has also been achieved by threading a polyfluorene through cyclodextrin rings, which was evidenced by blue-shifted emissions of the threaded polymers with respect to those of the unthreaded polymers.[10]

Organic boronic acids are very useful reagents in organic synthesis, particularly for obtaining structurally well-defined conjugated polymers through the Suzuki coupling reaction with arylhalides.[11a] The insolubility of the organoboronic acids after drying has often been encountered when dealing with these compounds, which is due to the dehydration upon heating and the formation of anhydride structures.[11b−e] When an organoboronic acid possesses di- or multi-boronic acid groups, cross-linked networks of the compound can be formed upon thermal treatment.[11e] In this study we have investigated the attachment of readily cross-linkable boronic acid groups to conjugated oligomers as a novel and effective approach to immobilizing the chromophores. Because these oligomers are easily purified by recrystallization or chromatography, highly pure compounds are readily obtained. This offers the cured oligomer films a higher chemical stability due to less impurities such as metal ions, which were usually introduced from the catalyst during the preparation and could further catalyze the oxidation of the polymers during operation.[6c] On the other hand, the use of a boronic acid group for cross-linking is also expected to resolve the issue of chain aggregation observed in polyfluorene. A series of novel structurally well-defined oligofluorenes possessing boronic acid end groups have therefore been designed and synthesized (see Scheme 1). The use of fluorene oligomers is based on several considerations. First, from the synthetic point of view, highly pure and monodispersed chromophores can be obtained, which would offer improved stability and sharper emission bands than those of their polymeric analogues. Second, oligofluorenes might prevent the undesirable increase in the effective conjugation length in the solid state that sometimes results in emission spectra with progressive red shifts.[3c,d] Furthermore, higher quantum efficiencies can be expected for oligofluorenes because shorter conjugation systems usually can trap or confine excitons to prevent their migration to quenching sites.[12] Our preliminary results indicate that these oligofluorenes are highly photoluminescent, processable by conventional spin-coating to fabricate uniform films, and cross-linkable under very mild conditions (60 °C under vacuum for 2 h) to form thermally and optically stable blue-light-emitting networks.

Experimental Section

Measurements. ^{1}H NMR spectra were obtained in $CDCl_3$, acetone-d_6, or toluene-d_8 on a 400 MHz Varian Unity Inova spectrometer. IR spectra were recorded on a Midac M1200-SP3 spectrophotometer. UV−vis absorption spectra were obtained on a Hewlett-Packard 8453 spectrophotometer. Fluorescence measurements were carried out on a Spex Fluorolog 3 spectrometer. Absorption maxima of compounds were used as the excitation wavelengths for the measurement. THF solutions of compounds with absorbances of 0.03−0.05 were deoxygenated prior to fluorescence measurement and the percentage fluorescence quantum yields Φ_{fl} ($\leq$10% error) were determined against 9,10-diphenylanthracene in cyclohexane (Φ_{fl} = 90%) at room temperature.[13] Polymer films with absorbances in a range of 0.3−0.6 were prepared on glass substrates by spin-coating of oligofluorene diboronic acids in THF (10 mg/mL) and were subjected to UV−vis and fluorescence measurements. The differential scanning calorimetry (DSC) analysis and the thermogravimetric analysis (TGA) were performed under a nitrogen atmosphere (50 mL/min) on a TA Instruments DSC 2920 and a TGA 2950 thermogravimetric analyzer, respectively, at heating rates of 10 °C/min (DSC) and 20 °C/min (TGA). The onset temperatures of melting on DSC curves are reported as the melting points (mp).

Materials. Triisopropyl borate and tetrakis(triphenylphosphine) palladium (0) ($Pd(PPh_3)_4$) were prepared according to literature methods.[14,15] Other starting materials were purchased from Aldrich and used without further purification.

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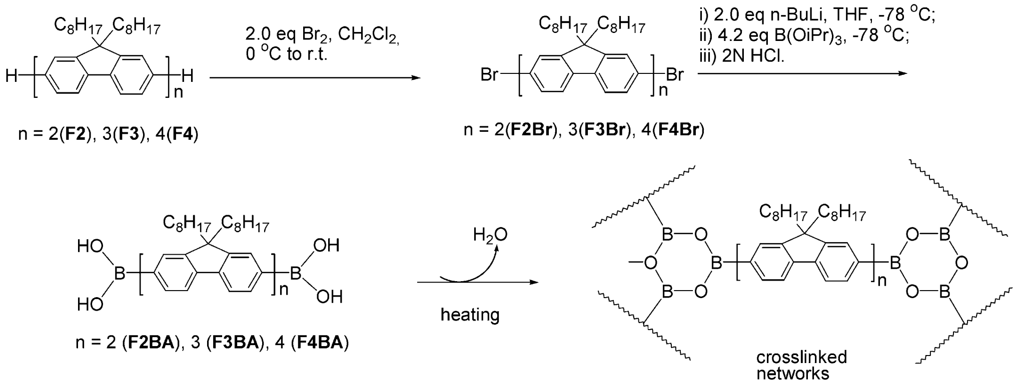
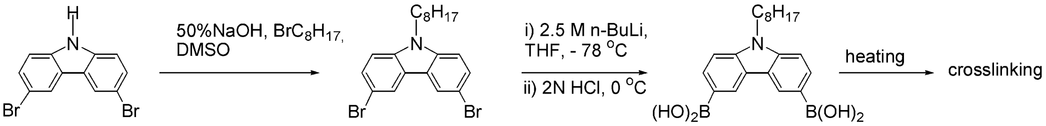
Scheme 1. Syntheses and Thermal Dehydration of the Diboronic Acids

1. Oligofluorene



2. Carbazole



Tetrahydrofuran (THF) and diethyl ether were dried over a Na/K alloy and distilled prior to use. 2,2′-Bis(9,9-dictylfluorenyl) (**F2**),[16–18] 2,2′-bis(7-bromo-9,9-dioctylfluorenyl) (**F2Br**),[17] and 2,2′-bis(7-dihydroxyboranyl-9,9-dioctylfluorenyl) (**F2BA**)[17] were prepared according to the reported methods.

2,2′:7′,2″-Ter(9,9-dioctylfluorene) (F3). To a 250-mL flask equipped with a condenser were added 2,7-dibromo-9,9-dicotylfluorene[17] (5.48 g, 10 mmol), 2-dihydroxyboranyl-9,9-dioctylfluorene[17] (9.13 g, 21 mmol), toluene (120 mL), and 2 M Na_2CO_3 solution (80 mL). The flask was then evacuated and filled with argon 3× to remove air from the system. The flask was then transferred to a glovebox under nitrogen where $Pd(PPh_3)_4$ (0.23 g, 0.2 mmol) was added. The flask was again briefly evacuated and filled with argon 3×. The mixture was heated to reflux and maintained for 48 h under an argon atmosphere. The resulting mixture was poured into a separation funnel and the organic layer was separated and dried over $MgSO_4$. Removal of the solvents by evaporation produced a brown viscous liquid. This liquid was dissolved in hexane and passed through a short silica gel column to remove the catalyst residue. The resultant solid, upon removal of solvents, was dissolved in CH_2Cl_2 and precipitated from methanol 3×. A pale yellow solid was obtained after drying under vacuum (8.72 g, 75%). ^{1}H NMR (in $CDCl_3$): δ 7.60–7.84 (m, 14H), 7.30–7.40 (m, 6H), 2.00–2.14 (m, 12 H), 1.02–1.24 (m, 60H), 0.64–0.86 (m, 30H). IR (KBr): 3059, 2954, 2926, 2854, 1610, 1465, 1451, 1377, 1254, 1101, 885, 817, 740 cm^{-1}. mp: 63–65 °C. UV–vis (in CH_2Cl_2): λ_{max} 352 nm.

7,7″-Dibromo-2,2′:7′,2″-ter(9,9-dioctylfluorene) (F3Br). To a solution containing **F3** (8.0 g, 6.85 mmol), iodine (5 mg, 0.02 mmol), and CH_2Cl_2 (100 mL) at 0 °C was added dropwise a bromine solution (2.19 g, 13.7 mmol in 10 mL CH_2Cl_2) over 15 min. The mixture was then allowed to warm to room temperature and stirred for 20 h in the absence of light. A 15% $NaHSO_3$ solution (50 mL) was then added, and the mixture was vigorously stirred for 30 min until the brown color disappeared. The organic layer was separated, washed with water 3×, and dried over $MgSO_4$. Evaporation of the solvent produced a light yellow viscous liquid. The crude product was dissolved in acetone (900 mL) and recrystallized at −40 °C 3× to give a white solid (7.82 g, 86%). ^{1}H NMR ($CDCl_3$): δ 7.80 (d, J 8.0 Hz, 2H), 7.74 (d, J 8.0 Hz, 2H), 7.57–7.67 (m, 10H), 7.48 (s, 2H), 7.45 (dd, J_1 8.0 Hz, J_2 2.0 Hz, 2H), 2.10 (m, 8H), 2.03 (m, 8H), 1.04–1.24 (m, 80H), 0.62–0.88 (m, 40H). IR (KBr): 2953, 2926, 2853,1455, 1405, 1377, 1256, 1062, 1001, 884, 811, 755, 722 cm^{-1}. mp: 77–78 °C. UV–vis (in CH_2Cl_2): λ_{max} 355 nm.

7,7″-Bis(dihydroxyboranyl)-2,2′:7′,2″-ter(9,9-dioctylfluorene) (F3BA). To a solution of **F3Br** (2.65 g, 2 mmol) in THF (20 mL) at −78 °C was added dropwise 2.5 M *n*-BuLi in hexane (1.76 mL, 4.4 mmol) over 15 min. The resulting mixture was stirred for 1 h while maintaining the temperature at −78 °C, after which triisopropylboronate (1.58 g, 8.4 mmol) was added and the mixture was stirred at −78 °C for an additional hour. The reaction mixture was then allowed to warm to room temperature and stirred for 15 h. The mixture was then cooled to 0 °C and 2 N HCl (10 mL) was added. After stirring for 30 min, the organic layer was separated using ether, washed with brine 3×, dried over $MgSO_4$, and filtered. Evaporation of the solvents gave a light yellow viscous liquid, which was precipitated from hexane to give a white solid. The solid was filtered, washed with hexane 3×, and dried briefly (30 min) under vacuum at room temperature. The resulting compound was a white solid (2.18 g, 86%). ^{1}H NMR (acetone-d_6/D_2O: v/v, 20/1): δ 7.99 (s, 2H), 7.89–7.95 (m, 6H), 7.86 (dd, J_1 4.8 Hz, J_2 1.6 Hz, 4H), 7.74–7.82 (m, 6H), 2.07–2.24 (m, 12H), 1.02–1.22 (m, 60H), 0.62–0.82 (m, 30 H). IR (KBr): 3429 (OH), 2953, 2926, 2854, 1608, 1460, 1413, 1331, 1256, 816 cm^{-1}. mp: 55.1 °C. UV–vis (in THF): λ_{max} 359 nm.

2,2′:7′,2″:7″,2‴-Quater(9,9-dioctylfluorene) (F4). This compound was prepared using **F2Br** (4.69 g, 5 mmol) and 2-dihydroxyboranyl-9,9-dioctylfluorene[17] (4.78 g, 11 mmol) under conditions similar to those used to prepare **F3**. The final reaction mixture was poured into a separation funnel, and the organic layer was separated and dried over $MgSO_4$. Removal of the solvents gave a brown viscous liquid which was dissolved

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in hexane and passed through a short silica gel column to remove catalyst residues. The viscous liquid (~6.0 g) was then dissolved in hot acetone (200 mL); the solution was cooled to room temperature and then to − 40 °C. A greenish solid was obtained upon recrystallization 4× (5.08 g, 65.3%). ^{1}H NMR ($CDCl_3$): 7.28−7.38 (m, aromatic protons, 6H), 7.58−7.85 (m, aromatic protons, 20H), 1.96−2.14 (m, α-methylene, 16H), 1.02−1.24 (m, 80H), 0.60−0.86 (m, 40H). IR (KBr): 3058, 3017, 2954, 2928, 2854, 1610, 1463, 1452, 1403, 1376, 1254, 1000, 885, 815, 740 cm^{-1}. UV−vis (in CH_2Cl_2): λ_{max} 363 nm.

7,7‴-Dibromo-2,2′:7′,2″:7″,2‴-quater(9,9-dioctylfluorene) (F4Br). This compound was prepared using **F4** (4.0 g, 2.57 mmol) and bromine (0.82 g, 5.14 mmol) following the procedure used in the preparation of **F3Br**. Recrystallization 3× using acetone (400 mL) at − 40 °C gave a greenish solid (3.34 g, 76%). ^{1}H NMR ($CDCl_3$): δ 7.45−7.85 (m, 24H), 1.92−2.16 (m, 16H), 1.02−1.26 (m, 80H), 0.62−0.88 (m, 40H). IR (KBr): 2953, 2926, 2853,1455, 1404, 1376, 1255, 1062, 1000, 885, 811, 756, 722 cm^{-1}. mp: 59−60 °C. UV−vis (in CH_2Cl_2): λ_{max} 366 nm.

7,7‴-Bis(dihydroxyboranyl)-2,2′:7′,2″:7″,2‴-quater(9,9-dioctylfluorene) (F4BA). The synthetic procedure used to prepare **F3BA** was followed using **F4Br** (1.40 g, 0.82 mmol) as the starting material. The resultant product was a light green solid (0.71 g, 53%). ^{1}H NMR (toluene-d_8/ acetone-d_6/D_2O, v/v, 20/5/1): δ 8.31 (s, 2H), 8.19 (dd, J_1 7.6 Hz, J_2 1.2 Hz, 2H), 7.89 (s, 6H), 7.66−7.80 (m, 14H), 2.06−2.20 (m), 0.76−1.20 (m). IR (KBr): 3434 (OH), 2953, 2926, 2854, 1608, 1459, 1412, 1331, 1255, 1000, 885, 814, 721 cm^{-1}. mp: 83.2 °C. UV−vis (in THF): λ_{max} 369 nm.

Results and Discussion

Materials Synthesis. Oligofluorenes carrying boronic acid groups at the 2- and 7-positions, **F2BA**, **F3BA**, and **F4BA**, were synthesized according to procedures outlined in Scheme 1. Octyl-substituted fluorene dimer (**F2**), trimer (**F3**), and tetramer (**F4**) were brominated using Br_2 in the presence of a catalytic amount of iodine in dichloromethane to afford dibromo compounds, **F2Br**, **F3Br**, and **F4Br**. Diboronic acids **F2BA**, **F3BA**, and **F4BA** were then prepared via lithiation of **F2Br**, **F3Br**, and **F4Br**, respectively, using 2.5 M *n*-BuLi at −78 °C in THF, followed by subsequent in-situ reaction with triisopropylboranate, and hydrolysis with 2 N HCl. After being dried under vacuum at room temperature, the compounds **F2BA**, **F3BA**, and **F4BA** were difficult to dissolve in dry solvents, presumably due to the formation of some cross-linked structures through partial dehydration of the boronic acid groups (confirmed by IR spectra as shown in Figure 1). However, when traces of water were added, they readily dissolved in solvents such as THF, acetone, and DMF. In the presence of water it would appear that the cross-linked linkages in these materials are hydrolyzed to release soluble free boronic acids. The resultant solubility of these compounds under these conditions facilitates the characterization of their chemical structures and the fabrication of films by solution casting. Although **F4BA** could be dissolved in wet acetone, the resultant transparent solution was found to be metastable and became cloudy within minutes, and eventually a white solid precipitated. When an equivalent amount of toluene was added to the mixture, however, the solid dissolved again. The ^{1}H NMR measurement of **F4BA** was therefore carried out in a solvent mixture containing toluene-d_8/ acetone-d_6/D_2O (v/v/v: 20/5/1). The above solubility changes noted for **F4BA** suggest that the intermolecular interactions within the solid **F4BA** are dominated by the dehydration between boronic acid groups. Once the dehydrated structure has been dissociated by water in the polar solvents, the hydrophobic moieties in **F4BA** start to self-assemble into aggregates, driven by the intermolecular van der Waals force. As will be discussed later, this dehydrated structure in these boronic acids presumably has the effect of overcoming the weaker intermolecular $\pi-\pi$ interaction.

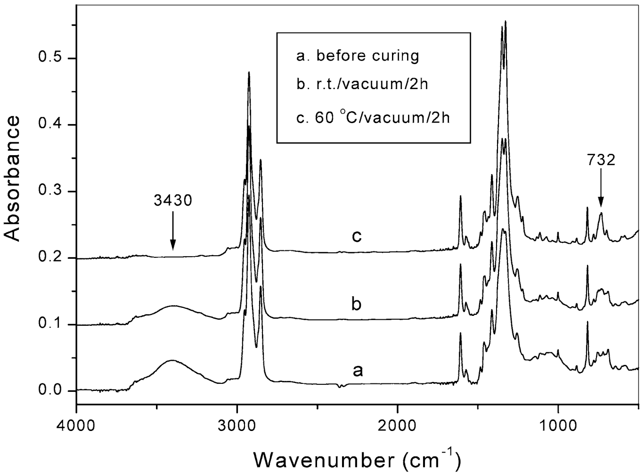

Figure 1. FT-IR spectra of the as-prepared and cured **F2BA** films on KBr disks. From a to c, the spectrum is upshifted by 0.1 successively.

Cross-Linking Reaction. Thin films of oligofluorene diboronic acids on KBr disks were prepared by casting solutions of **F2BA**, **F3BA**, and **F4BA** in THF followed by the evaporation of the solvent in air. The as-prepared films were immediately subjected to IR measurements. These films were then cross-linked in a vacuum oven at different temperatures. As shown in Figure 1, the IR absorption of the BO−H groups of **F2BA** at 3430 cm^{-1} virtually disappeared after heating at 60 °C for 2 h. At the same time a new absorption peak at 732 cm^{-1} appeared which could be assigned to the out-of-plane vibration of the boroxine structure. Meanwhile, the strong asymmetric B−O stretching peak around 1330−1340 cm^{-1} remained after heating.[19] Similar IR results have been observed for **F3BA** and **F4BA** (spectra not shown). These changes in the IR spectra strongly suggest the formation of cross-linked networks via the formation of six-membered boroxine rings (Scheme 1). It was noted that this dehydration could also occur at room temperature (Figure 1), which explains the poor solubility of these boronic acids after drying. The ease of this dehydration reaction in the solid state under such mild reaction conditions might be explained by the close proximity of boronic acid groups to each other due to hydrogen bonding. As mentioned above, these cross-linked structures can be readily hydrolyzed in the presence of wet polar solvents such as THF and acetone, but they are insoluble in water and in anhydrous organic solvents alone. This property offers excellent processing capabilities for these materials, facilitating the fabrication of multilayered films by the use of

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(19) (a) *The Organic Chemistry of Boron*; Gerrard, W., Ed.; Academic Press: London, 1961; p 223. (b) *Tables of Spectral Data for Structure Determination of Organic Compounds*; Biemann, K., Trans.; Springer-Verlag: New York, 1989.

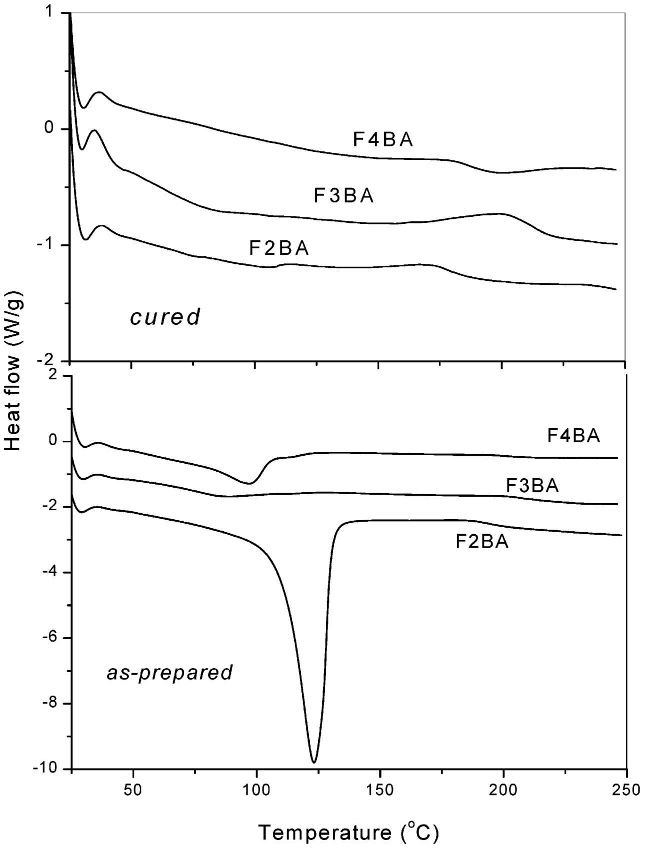

Figure 2. DSC curves (first heating run) of the as-prepared samples (bottom) and the cured samples (top) of oligofluorene diboronic acids at a heating rate of 10 °C/min under nitrogen (50 mL/min). Curing condition: 110 °C under vacuum for 2 h.

anhydrous solvents. This property should also pose no problem for these materials in applications requiring a dry atmosphere such as LEDs.

Thermal Properties. DSC and TGA analyses were first performed on the as-prepared samples of **F2BA**, **F3BA**, and **F4BA**. The DSC curve of **F2BA** on the first heating scan (r. t. −250 °C) shows a large endothermic peak at 123 °C (Figure 2), which reflects the melting and partial dehydration of the boronic acid groups (confirmed by TGA analysis). Similarly, the **F3BA** and **F4BA** samples exhibited broad melting processes that peaked at 86 and 97 °C, respectively. However it is noted that their heat capacities are much lower than that of **F2BA**, suggesting that these materials have lower degrees of crystallinity. On the other hand, after being cured at 110 °C under vacuum for 2 h, the cured samples of **F2BA**, **F3BA**, and **F4BA** showed no melting points during the DSC scans on the first heating. Only slight transitions with onset temperatures of 173 °C for **F2BA**, 202 °C for **F3BA**, and 181 °C for **F4BA** were observed. They were attributed to the glass transition temperatures (T_gs). The high T_gs of these materials suggest that the thermal treatment under mild conditions (110 °C under vacuum for 2 h) produced thermally stable amorphous polymer networks. Second DSC heating scans, on both the as-prepared and cured samples, no longer exhibit any transitions below 250 °C, indicating that the dehydration reaction was completed during the first heating scan and the resulting networks have even higher cross-linking densities than those of the cured samples.

The TGA analysis of **F2BA** shows that this compound starts to lose weight as soon as heating commences, with a rapid loss of weight occurring at 114 °C due to the dehydration of boronic acid groups (Figure 3). The dehydration is almost completed once the temperature has reached 150 °C, and the weight remains relatively constant up to 363 °C when the sample starts to decompose. Similar trends were observed for the other two samples, **F3BA** and **F4BA**, which show a first transition (dehydration) at 72 and 82 °C, and a second transition (decomposition) at 414 and 408 °C, respectively. The weight losses due to the dehydration for

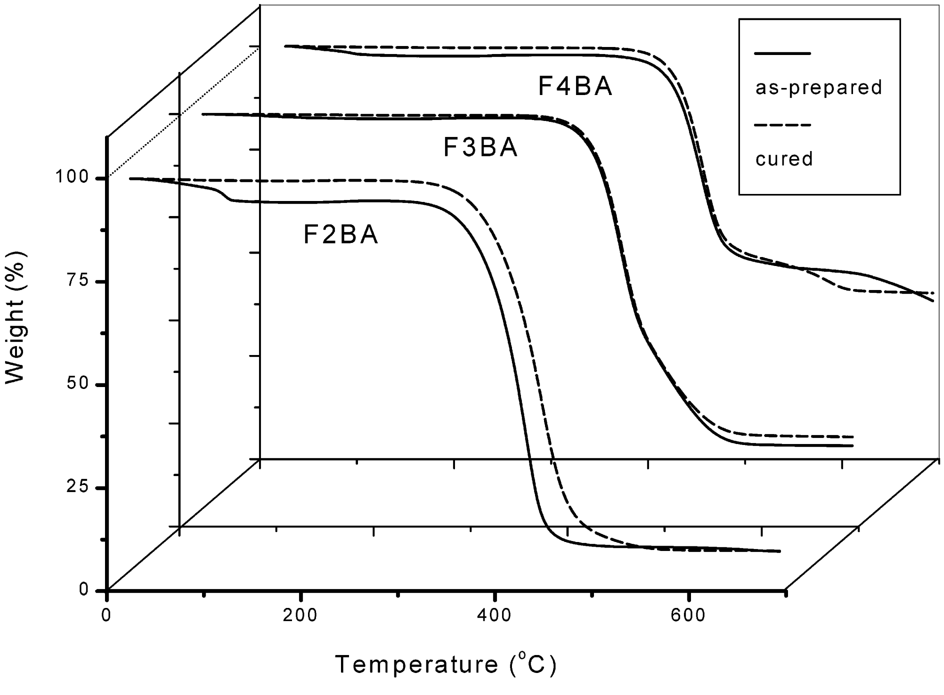

Figure 3. TGA weight loss curves for the as-prepared and the cured **F2BA**, **F3BA**, and **F4BA** samples at a heating rate of 20 °C/min under nitrogen (50 mL/min). Curing condition: 110 °C under vacuum for 2 h.

Table 1. Photophysical Properties of Oligofluorene Diboronic Acids

				films			
	solution			as-prepared		cured[a]	
sample	$\lambda_{\mathrm{max,\,abs}}$ nm	$\lambda_{\mathrm{max,\,em}}$ nm	Φ_{fl}, %	$\lambda_{\mathrm{max,\,abs}}$ nm	$\lambda_{\mathrm{max,\,em}}$ nm	$\lambda_{\mathrm{max,\,abs}}$ nm	$\lambda_{\mathrm{max,\,em}}$ nm
F2BA	341	376 397 420(s)	85	341	387(s) 406 429(s)	349	392(s) 409 433(s)
F3BA	359	402 424 451(s)	96	359	409 429	363	411 430
F4BA	369	413 436 465(s)	98	368	415 438 469(s)	369	416 438 473(s)

[a] Conditions: 60 °C under vacuum for 2 h.

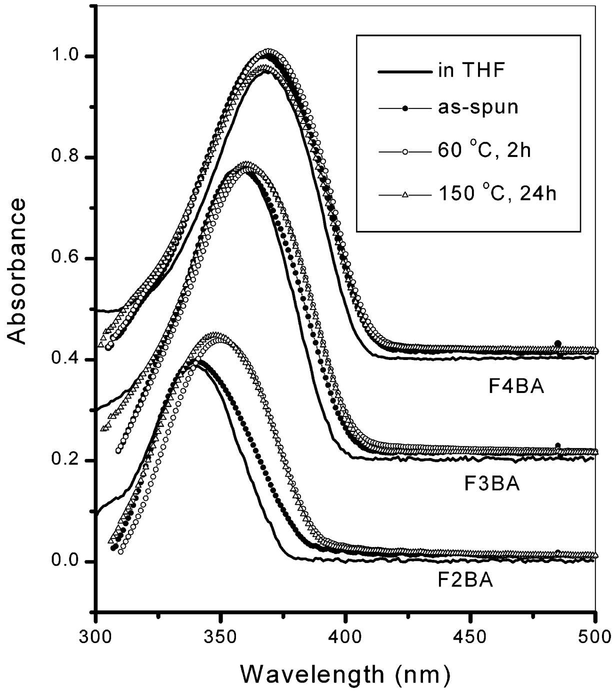

Figure 4. UV−vis absorption spectra of **F2BA**, **F3BA**, and **F4BA** in THF solution and in film. The film spectra were taken successively after the film was spun (as-spun), after it was heated at 60 °C for 2 h, and then after it was heated at 150 °C for 24 h. The solution spectrum was magnified in intensity in order to compare with the film spectra. From F2BA to F4BA, the spectra were upshifted by 0.2 successively.

F2BA, **F3BA**, and **F4BA** were 5.6%, 1.1%, and 2.3%, respectively. These values show some discrepancies with the calculated values (4.2%, 2.7%, and 2.2%, respectively), probably due to slight variations in the drying conditions used in their synthesis.

All three cured samples showed no weight losses prior to decomposition, indicating that complete dehydration of the samples had occurred under the chosen curing conditions (110 °C under vacuum for 2 h). The 5% weight loss temperatures ($T_{d,5\%}$s) for the cured **F2BA**, **F3BA**, and **F4BA** were 370, 417, and 420 °C, respectively. These results demonstrate the high thermal stability of these cross-linked materials.

Photophysical Properties. The UV−vis absorption spectrum of **F2BA** in THF has a red-shifted absorption maximum $\lambda_{\mathrm{max,abs}}$ at 341 nm, compared with those of its precursor dimers **F2** ($\lambda_{\mathrm{max,abs}}$ 329 nm) and **F2Br** ($\lambda_{\mathrm{max,abs}}$ 336 nm) (Figure 4 and Table 1). This red shift can be accounted for by the involvement of the boronic acid groups in the main chain conjugation. This arises because the B−O bond has been reported to have some double-bond character due to back coordination of the oxygen to the boron.[20] The samples **F3BA** and **F4BA** showed similar red-shifts in their $\lambda_{\mathrm{max,abs}}$ values (359 and 369 nm) compared with those of their corresponding precursors **F3**/**F3Br** (352 nm/355 nm) and **F4**/**F4Br** (363 nm /366 nm), which are close to the reported values of the fluorene trimers and tetramers despite a slight difference of the substituted groups at the 9-positions of fluorene.[21] However, in these cases the contribution from the boronic acid groups appears to be less evident because of the increased lengths of the backbone. The photoluminescence spectrum of **F2BA** in THF exhibited two vibronic peaks at 376 and 397 nm, and a shoulder at 420 nm (Figure 5). Meanwhile **F3BA** has two emission peaks at 402 and 424 nm, and a shoulder at 451 nm. Emission peaks for **F4BA** appeared at 413 and 436 nm (with a shoulder at 465 nm), which are very close to those reported for polyfluorenes (415 and 439 nm).[17] The fluorescence yield (Φ_{fl}) in solution increases as the conjugation length increases, with the values of 85% (**F2BA**), 96% (**F3BA**), and 98% (**F4BA**). These values are higher than those reported for most polyfluorenes. This phenomenon might be explained by the better confinement of excitons[12] in these conjugated oligofluorenes.

Solutions of **F2BA**, **F3BA**, and **F4BA** were prepared by dissolving these compounds in THF that contained traces of water, drying over $MgSO_4$, and filtering. Spin-coating these solutions onto glass substrates gave uniform, transparent thin films, despite the fact that these compounds showed some crystallinity in their powdery state. The as-spun films of **F2BA**, **F3BA**, and **F4BA** displayed absorption peaks at 341, 359, and 368 nm, respectively, almost the same as those measured in solutions (Figure 4 and Table 1). Under UV irradiation, **F2BA** films emitted violet-blue light, whereas films of **F3BA** and **F4BA** emitted bright blue light. Emission maxima ($\lambda_{\mathrm{max,em}}$) of these compounds bathochromically shifted 9 nm (from 397 to 406 nm) for **F2BA**, 7 nm (from 402 to 409 nm) for **F3BA**, and 2 nm (from 413 to 415 nm) for **F4BA** (Figure 5 and Table 1). There is not any long wavelength emission peak appeared in the region of 500−600 nm. After being cured at 60 °C under vacuum for 2 h, the $\lambda_{\mathrm{max,abs}}$ of these films red-shifted 8

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[20] (a) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 286. (b) *The Organic Chemistry of Boron*; Gerrard, W., Ed.; Academic Press: London, 1961; p 105.

[21] (a) Klaerner, G.; Miller, R. D. *Macromolecules* **1998**, *31*, 2007. (b) Lee, S. H.; Tsutsui, T. *Thin Solid Film* **2000**, *363*, 76.

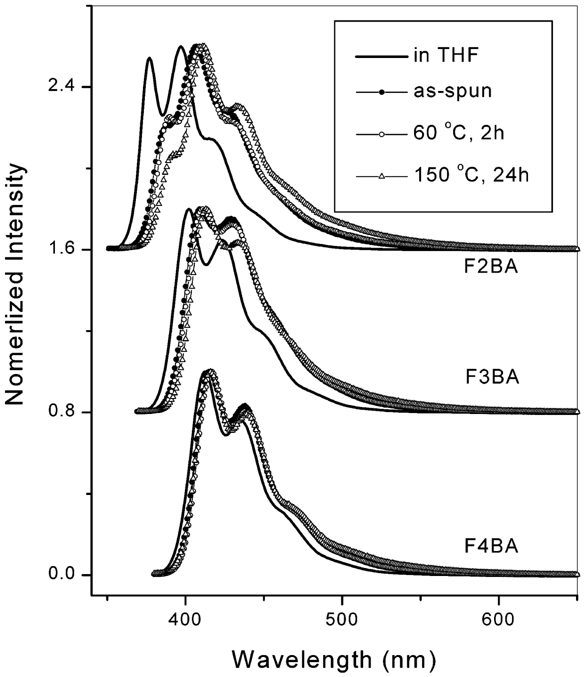

Figure 5. Photoluminescence spectra of (a) **F2BA**, (b) **F3BA**, and (c) **F4BA** in THF solution and in film. The film spectra were taken successively after the film was spun (as-spun), after it was heated at 60 °C for 2 h, and then after it was heated at 150 °C for 24 h. From F4BA to F2BA, the spectra were upshifted by 0.8 successively.

nm for **F2BA**, 4 nm for **F3BA**, and 1 nm for **F4BA**. Slight red-shifts in the $\lambda_{\max,\mathrm{em}}$ of the fluorescence spectra were also observed for these cured films (3 nm for **F2BA**, 2 nm for **F3BA**, and 1 nm for **F4BA)**. However, in all cases there were still no signs of long wavelength emissions. The red-shifts in the absorption and emission were assumed to be the result of the slight increase in conjugation. The weakly conjugated boroxine rings[22] that formed during the curing treatment might bridge the main chain π-systems. Prolonged curing (60 °C, 4 h) or heating at a higher temperature (120 °C, 2 h) did not appear to cause any appreciable changes in the UV−vis and fluorescence spectra of these compounds. Even after heating at 150 °C for 24 h, no noticeable changes appeared in the UV−vis spectra for any of the **F2BA**, **F3BA**, and **F4BA** films. Minor changes in the relative intensities of emission peaks were observed for **F2BA** and **F3BA** films, but the peaks were located at almost the same positions as before heating. These changes may be due to further formation of boroxine structures at elevated temperatures that resulted in a slightly more extended conjugation system. Among these three samples, **F4BA** exhibited the highest spectral stability, showing no appreciable changes in UV−vis and fluorescence spectra upon thermal treatment (Figures 4 and 5). The absence of long wavelength emissions in the region of 500−600 nm for these oligofluorene networks clearly suggests a significant improvement in color stability compared to that of polyfluorene. This may be attributed to improved chemical stability due to the higher purity of the oligomers, or to the reduced chain aggregation by cross-linking. It is worth noting that a similar result has also been obtained even when the films were cured in air at 110 °C for 2 h, indicating these materials are highly oxidative stable.

Electroluminescence (EL) Properties of LED Devices. A double-layer device has been designed for studying the EL properties of the oligofluorene diboronic acids using a carbazole compound for the hole transporting layer. Therefore, 3,6-bis(dihydroxyboranyl)-9-octylcarbazole (**CzBA**) was designed and synthesized as a hole-transporting material (Scheme 1). The IR study indicated that the dehydration of **CzBA** is very similar to that of **F2BA** as evidenced by IR measurements as shown in Figure 1. Though the IR study indicates that the dehydration can be completed by heating the samples at 60 °C under vacuum for 2 h, an actual dehydrating condition of 130 °C under vacuum for 2 h was used for curing the diboronic acid layers in the device fabrication in order to ensure a complete dehydration. The solvent resistance of the cured films was tested by rinsing the films with solvent on a spin-coater. As mentioned above, these cross-linked structures can be hydrolyzed only in wet polar solvents such as THF and acetone. When the cured film was rinsed with nonpolar solvents such as toluene, or dry polar solvent such as THF, or even water, no thickness change was observed after rinsing. However, if the cured film was rinsed with wet THF, a significant change in thickness was observed. Therefore, in the device fabrication, the second layer film was spin-coated from a dried THF solution under the protection of nitrogen. The LED devices were fabricated as follows. The **CzBA** layer (∼140 nm) on ITO was prepared by spin-coating a **CzBA** solution (15 mg/mL in THF). The film was cured at 130 °C for 2 h and cooled slowly to room temperature. The light-emitting layer (∼140 nm) was then mounted by spin-coating an **F3BA** or **F4BA** solution (15 mg/mL in THF) on the cured **CzBA** layer. The sample was once again cured at 130 °C for 2 h. The thickness of the **CzBA/F3BA** (or **F4BA**) double layer was ∼280 nm, which is equal to the sum of individual **CzBA** and **F3BA** (or **F4BA**) layers prepared separately. This indicates that the **CzBA** layer survived during second layer spin-coating and this procedure is suitable for fabrication of double- (or multi-) layered devices. Finally, an Mg/Ag (9:1) alloy layer was deposited on the **F3BA** (or **F4BA**) layer as a cathode. For comparative purposes, a single-layer device with **F3BA** but without the **CzBA** layer was also fabricated. The electroluminescence spectra and luminance/current curves for the devices made with **F3BA** are shown in Figure 6. The EL emission peaks due to 0−1 interchain singlet transitions for **F3BA** and **F4BA** are 432 and 440 nm, respectively, very close to their PL values (430 and 438 nm). However, the 0−0 transitions observed in the EL spectra were less pronounced than those in the PL spectra for reasons still unknown. No obvious emission peaks were noted in the region of 500−600 nm, although the intensity in that region is somewhat higher than that of the corresponding PL spectra. The maximum luminance of the **CzBA/F3BA** device was 259 cd/m^2 at an electric field strength of 21×10^5 V/cm, whereas the value for the **CzBA/F4BA** device was 90 cd/m^2. The luminance efficiencies were calculated to be 0.1 cd/A for **CzBA/F3BA** and 0.05 cd/A for **CzBA/F4BA** devices, and these values are steady in the most voltage range. However, the LED device

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(22) Ring, M. A.; Koski, W. S. *J. Chem. Phys.* **1961**, *35,* 381.

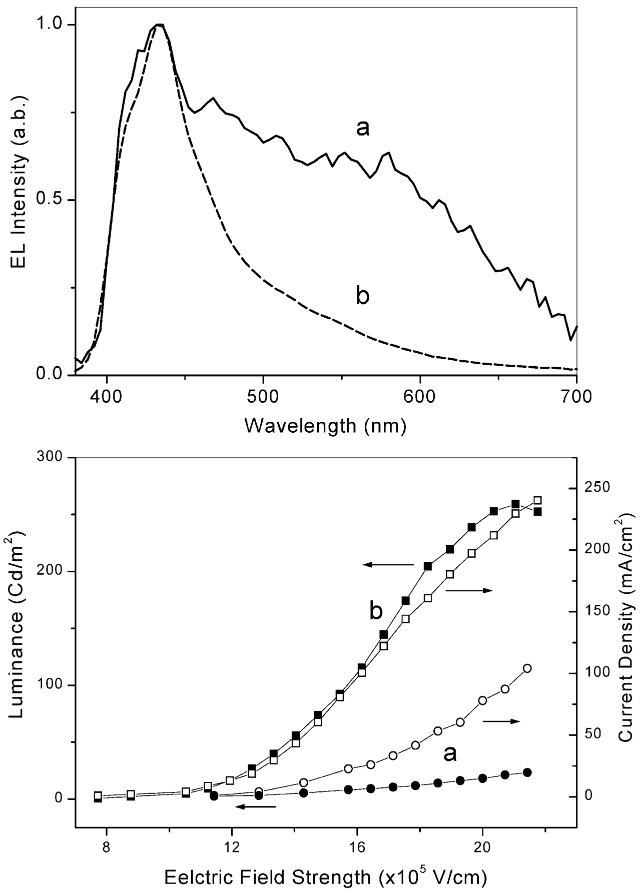

Figure 6. Electroluminescent spectra (top) and luminance/current density curves (bottom) of LED devices (a) ITO/**F3BA**/Mg:Ag and (b) ITO/**CzBA**/**F3BA**/Mg:Ag.

with an ITO/**F3BA**/Mg:Ag configuration showed very poor performance as shown in Figure 6. The maxiumum luminance is only about 10 cd/m^2 associated with a very broad emitting peak from 400 to 700 nm with the efficiency of 10× less than that of the double-layer device. The great current density and the low efficiency of this device indicate that the poor performance is related to the mismatch of hole and electron injected into the film. This leads to a high charge density in the emitting layer and causes oxidation of the materials, which could be the cause for a very broad EL peak from the single-layer device. On the other hand, this result suggests that the **CzBA** layer plays an important role as a hole-transportation medium in the double-layer devices. Although the performances of these double-layered devices are still not satisfactory, these preliminary results indicate that the approach of using thermally cross-linkable boronic acids as the charge-transporting layer and light-emitting layer in a LED could facilitate the device fabrication and result in improved device performance.

Conclusion

A novel approach based on the thermal dehydration of oligofluorene diboronic acids via the formation of boroxine linkages has been proposed to offer an easy approach to fabricate multilayer LED devices, and to resolve the problems associated with efficiency decrease accompanied with the emerging of long wavelength emission that has often been observed for polyfluorenes as a blue-light-emitting material. The oligofluorene diboronic acids, **F2BA**, **F3BA**, and **F4BA**, were thus designed and synthesized. These compounds are readily soluble in organic solvents such as THF, acetone, and DMF and can be easily fabricated into uniform thin films by spin-coating of their THF solutions onto substrates. The thin films can then be conveniently cross-linked using mild conditions (60−130 °C under vacuum for 2 h) to form solvent-resistant and thermally stable amorphous polymeric networks (T_g, 173−202 °C; $T_{d,5\%}$, 363−420 °C). The absorption and emission spectra of these thin films were also found to be thermally stable, showing no long wavelength emissions after being heated at 150 °C for 24 h. The fabrication of double layered LED devices using **F3BA** or **F4BA** as the light-emitting layer and **CzBA** as a hole-transporting layer has been demonstrated. The electroluminescence properties of these materials suggested that the **CzBA** layer works as hole-transporting layer, while the **F3BA** (or **F4BA**) works as the blue-light-emitting layer. Efforts to improve device performance continue with the focus on the role of the chemical structure of the hole-transporting layer and adding an appropriate electron-transporting layer.

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