

# Multi-H Shaped Macrocylic Oligomers Consisting of Triphenylamine and Oligofluorene: Synthesis and Optoelectronic Properties

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Novel multi-H shaped macrocyclic oligomers ((TPAF<sub>3</sub>)<sub>3</sub> and (TPAF<sub>5</sub>)<sub>3</sub>) were designed and synthesized for use as hole-transporting emitters in blue-light-emitting diodes (LEDs). In the produced macrocyclics, three triphenylamine units are connected in series to form a macrocyclic core through the C-9's of the central fluorene units of three surrounding oligofluorenes, which, like rigid rods, stick out of the ring plane in both sides. This specific structure renders the macrocyclics better photoluminescence (PL) stabilities and lower crystallization tendencies than polyfluorenes and excellent optoelectronic properties. The macrocyclics emit deep blue fluorescence with high efficiencies both in solutions and thin films ( $\Phi_{\text{pl-film}} = 57\%$  for (TPAF<sub>3</sub>)<sub>3</sub> and 52% for (TPAF<sub>5</sub>)<sub>3</sub>). (TPAF<sub>5</sub>)<sub>3</sub> films are stable against both electrochemical oxidation and reduction, with CV curves remaining unchanged in 10 successive potential scans. High-efficiency blue-light-emitting diodes were fabricated using the macrocyclics as the hole-transporting emitting layer. The device structure used in this study is ITO/(TPAF<sub>3</sub>)<sub>3</sub> or (TPAF<sub>5</sub>)<sub>3</sub>/TPBI/LiF/Al, where TPBI, 1,3,5-tris(*N*-phenylbenzimidazol-2-yl) benzene, is a morphologically stable material functioning as a hole-blocking/electron-transporting layer. The (TPAF<sub>5</sub>)<sub>3</sub>-based devices displayed a low turn-on voltage of 4 V and a maximum luminance of 1716 cd/m<sup>2</sup> at a voltage of 14.1 V; the (TPAF<sub>3</sub>)<sub>3</sub>-based devices gave 901 cd/m<sup>2</sup> at 13.0 V. The maximum luminous efficiencies of the (TPAF<sub>3</sub>)<sub>3</sub>- and (TPAF<sub>5</sub>)<sub>3</sub>-based devices reached 0.63 cd/A at 187 cd/m<sup>2</sup> and 0.93 cd/A at 340 cd/m<sup>2</sup>, respectively.

## Introduction

Blue-light-emitting diodes (LEDs) fabricated from polyfluorenes have shown poor stabilities, with a drastic loss in quantum yield and the appearance of an undesired green emission after a short period of operation. The origin of this green emission has been a subject of intensive investigation for a long time. It was attributed to both the excimer/interchain aggregates and the keto defects in the polymer backbone.<sup>1</sup> However, recent results revealed that the keto defects that originated from photo- and/or electrooxidative degradation of 9,9-dialkylated polyfluorenes were mainly responsible for this green emission.<sup>2</sup> It was found that this

green emission could be suppressed by incorporating hole-transporting materials with the polyfluorenes. For example, Scherf and his co-workers have shown that the end-capping or blending polyfluorenes with triphenylamine moieties or compounds can almost completely suppress this green emission.<sup>3</sup>

Monodisperse conjugated oligomers exhibit many attractive characteristics such as well-defined conjugation lengths and molecular structures, ease of purification, characterization, and solution processing. Moreover, recent rapid development of new synthetic methodologies makes it possible to design a variety of monodisperse oligomers, permitting efficient color and energy level tuning through the control of effective conjugation length as well as the introduction

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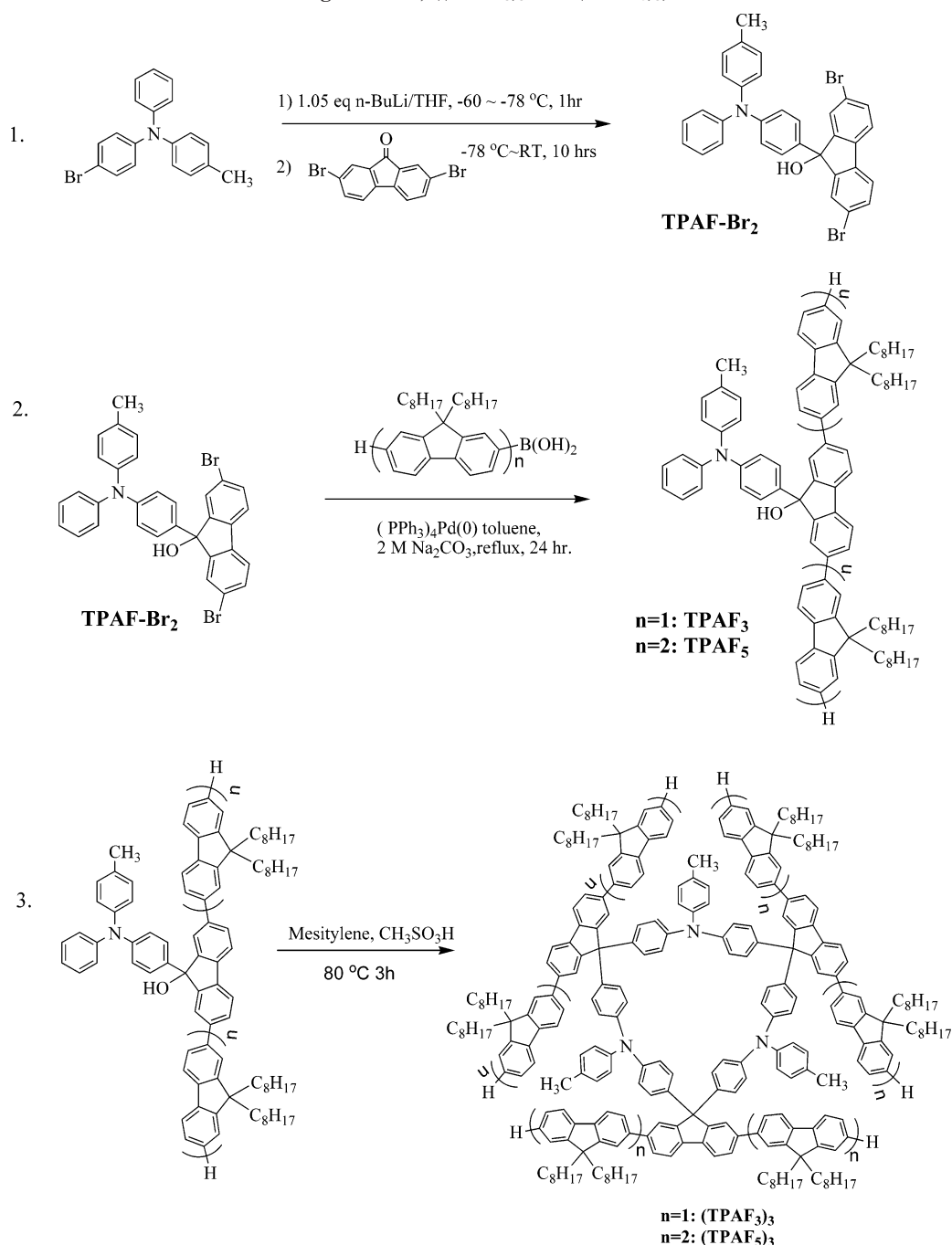
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**Scheme 1. Synthetic Route for the Preparation of the Multi-H Shaped Macrocyclic Oligomers Consisting of Triphenylamine and Oligofluorene, ((TPAF<sub>3</sub>)<sub>3</sub> and (TPAF<sub>5</sub>)<sub>3</sub>)**

of electron-donating and -withdrawing moieties into the parent  $\pi$ -conjugated systems.<sup>4</sup> Therefore, monodisperse conjugated oligomers have recently become a subject of intense study for optoelectronic applications,<sup>5–7</sup> and have been employed as ideal models<sup>8</sup> to understand the funda-

mental properties of the polydisperse polymeric analogues. A number of monodisperse oligofluorenes were synthesized as blue-light-emitting materials, aimed at eliminating the green emission.<sup>9</sup> For example, Cao et al. synthesized extended  $\pi$ -conjugated dendrimers and star-shaped molecules;<sup>9e,f</sup> Lai et al. synthesized six-arm triazatruxenes;<sup>9a</sup> Liu et al. reported a series of Si-based tetrahedral luminescent materials<sup>9g</sup> and Shih et al. designed and synthesized a series of carbazole/fluorene hybrids.<sup>9h</sup>

In this study, we designed and synthesized two novel multi-H shaped macrocyclic oligomers ((TPAF<sub>3</sub>)<sub>3</sub> and (TPAF<sub>5</sub>)<sub>3</sub>) consisting of triphenylamine and oligofluorene by

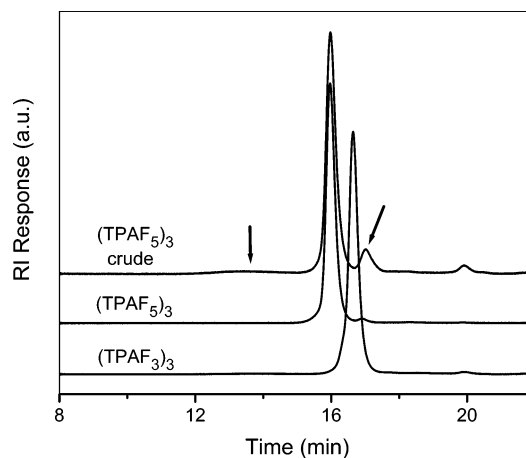
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combining the advantages of triphenylamine moieties for suppressing the green emission of polyfluorenes and the feasibility of monodisperse oligomers in purification, solution processing, and property tuning. In these macrocyclics, three triphenylamine units are connected in series to form a cyclic core through the C-9's of the central fluorene units of three surrounding oligofluorenes. These rodlike oligofluorenes intercept the ring plane to form a rigid three-dimensional structure, which is expected to afford the resulting macrocyclics a high steric hindrance for close interchain packing, and thus reduces their crystallization tendency. In fact, the PL spectra of  $(\text{TPAF}_3)_3$  and  $(\text{TPAF}_5)_3$  thin films showed only little change upon annealing in a vacuum at 100 °C for 24 h, indicating a better PL stability than polyfluorenes. The LED devices with configuration of ITO/ $(\text{TPAF}_5)_3$ /TPBI/LiF/Al demonstrated a pure blue emission with a maximum luminance and current efficiency of 1716 cd/m<sup>2</sup> at 14.1 V and 0.93 cd/A at 340 cd/m<sup>2</sup>, respectively.

## Results and Discussion

**Synthesis and Characterization.** The synthetic procedures used to prepare macrocyclic oligomers  $(\text{TPAF}_3)_3$  and  $(\text{TPAF}_5)_3$  are outlined in Scheme 1. First, *N*-(4-bromophenyl)-*N*-(4-methylphenyl) aniline was reacted with *n*-BuLi in tetrahydrofuran at −78 °C, followed by the addition of 2,7-dibromo-fluorenone to result in  $\text{TPAF-Br}_2$ . Then  $\text{TPAF-Br}_2$  was reacted with 9,9-di-*n*-octylfluorenyl-2-boronic acid, or 9,9,9',9'-tetra-*n*-octyl-2,2'-bifluorenyl-7-boronic acid, using a Suzuki coupling reaction in a mixture of toluene and a 2 M sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) aqueous solution (4/3, v/v). Tetrakis(triphenylphosphine) palladium(0),  $\text{Pd}(\text{PPh}_3)_4$ , was used as a catalyst, and tricaprylmethylammonium chloride (Aliquat 336) was used as a phase-transfer catalyst. The mixture was refluxed with stirring for 24 h to offer the monomer  $\text{TPAF}_3$  or  $\text{TPAF}_5$ . The multi-H shaped macrocyclics,  $(\text{TPAF}_3)_3$  and  $(\text{TPAF}_5)_3$  were then prepared by a self-condensation reaction of these monomers in mesitylene solution at 80 °C for 3 h in the presence of methylsulfonic acid. This reaction follows the aromatic electrophilic substitution mechanism. The para-H on the triphenylamine unit of the monomer is very reactive, because of the electron-donating property of the amino group, and reacts with the fluorenyl group, which is a strong alkylating reagent, for this self-condensation by the Friedel–Crafts procedure. This reaction potentially gives a series of macrocyclic oligomers with different ring sizes as  $(\text{TPAF}_m)_2$ ,  $(\text{TPAF}_m)_3$ ,  $(\text{TPAF}_m)_4$ ,



**Figure 1.** SEC spectra of the crude and purified samples of  $(\text{TPAF}_5)_3$  and purified  $(\text{TPAF}_3)_3$ .

through  $(\text{TPAF}_m)_n$  (where  $m = 3$  or  $5$ ) and linear polymers. However, the smallest possible macrocyclic,  $(\text{TPAF}_m)_2$ , contains only 4  $\text{sp}^3$  hybridized atoms in the ring (cf. cyclobutane) so the ring has a tremendous internal strain, and thus this macrocyclic has a low possibility of being formed in the reaction. On the contrary, the macrocyclic trimer (cf. cyclohexane) contains 6  $\text{sp}^3$  hybridized atoms and will be favorably formed. In addition, a very low monomer concentration ( $\sim 1\%$ ) has been used for the reaction, which favors the formation of smaller cyclic oligomers.<sup>10</sup> Consequently, our reaction condition gives the trimer,  $(\text{TPAF}_m)_3$ , as the major product.

The crude product from the self-condensation of  $\text{TPAF}_5$  was analyzed by the size exclusion chromatography (SEC) and MALDI-TOF mass spectroscopy. The SEC curve shown in Figure 1 displays a major narrow peak at 15.95 min, in addition to a secondary narrow peak at 17.01 min and a very small and broader peak around 13.62 min. The major peak has a  $M_n$  of 6300 Da with a very low  $M_w/M_n$  value (1.02), and the secondary peak has a  $M_n$  of 3500 Da. Because the  $M_n$  from SEC analysis is a polystyrene equivalent value, it is impossible to assign these peaks on the basis of the SEC data alone. Therefore, this crude product was also analyzed by MALDI-TOF mass spectroscopy. A major peak at 5924  $m/z$  and a secondary peak at 3949  $m/z$  present in the mass spectrum (not shown), corresponding to the macrocyclic trimer and dimer, respectively. Therefore, the major and the secondary peaks in both SEC curve and mass spectrum can be assigned to  $(\text{TPAF}_5)_3$  and  $(\text{TPAF}_5)_2$ , respectively, whereas the small and broader peak is attributed to the polymer formed in the reaction. This result indicates that  $(\text{TPAF}_5)_3$  is the predominant product from this reaction with 82% integrated intensity of the SEC curve. It is interesting to note that even though the macrocyclic dimer has a very high internal strain in the macrocyclic core, it was still produced from this reaction in a content of about 6% of the total materials, whereas no linear dimer and trimer were detected in the mass spectrum. This result indicates that the cyclization potential in this reaction is very high under the used reaction condition.

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**Table 1. Thermal and Optical Properties of (TPAF<sub>3</sub>)<sub>3</sub> and (TPAF<sub>5</sub>)<sub>3</sub>**

polymers	$T_g$ (°C)	$T_c$ (°C)	$T_m$ (°C)	$T_{d5\%}$ (°C)	UV $\lambda_{max}$ (nm)	film PL $\lambda_{em}$ (nm)	$\varphi_f$
POF	51	113	159	418	385	422, 447, 478	0.46
(TPAF <sub>3</sub> ) <sub>3</sub>	35	169	185	400	341	402, 424	0.57
(TPAF <sub>5</sub> ) <sub>3</sub>	34	n.a.	n.a.	408	367	416, 439	0.52

**Table 2. Electrochemical Properties of (TPAF<sub>3</sub>)<sub>3</sub> and (TPAF<sub>5</sub>)<sub>3</sub>**

polymers	$E_p'$ (V) <sup>a</sup>	$E_n'$ (V) <sup>a</sup>	$E_{HOMO}$ (eV) <sup>b</sup>	$E_{LUMO}$ (eV) <sup>b</sup>	$E_g$ (eV) <sup>c</sup>
POF	1.25	-2.00	-5.63	-2.38	3.25
(TPAF <sub>3</sub> ) <sub>3</sub>	0.65	-2.12	-5.03	-2.26	2.77
(TPAF <sub>5</sub> ) <sub>3</sub>	0.68	-2.10	-5.06	-2.28	2.78

<sup>a</sup> Onset oxidation (p-doping) and reduction (n-doping) potentials versus an Ag quasi-reference. <sup>b</sup> Estimated from the onset oxidation and reduction potential by using  $E_{HOMO} = -(E_p' + 4.38)$  eV and  $E_{LUMO} = -(E_n' + 4.38)$  eV. <sup>c</sup> Electrochemical band gaps determined using  $E_g = E_{HOMO} - E_{LUMO}$ .

The crude products of both (TPAF<sub>3</sub>)<sub>3</sub> and (TPAF<sub>5</sub>)<sub>3</sub> were purified by column chromatography on silica gel with an eluent of dichloromethane/petroleum ether (1/4, v/v, for (TPAF<sub>3</sub>)<sub>3</sub> and 1/5 for (TPAF<sub>5</sub>)<sub>3</sub>). The purified samples were characterized by SEC analysis and the results are compared with that of the crude product of (TPAF<sub>5</sub>)<sub>3</sub> in Figure 1. It is clear that this purification successfully removed the polymeric impurity and most of the macrocyclic dimer, leading to a clean and narrow peak with a  $M_w/M_n$  of 1.02 in the SEC spectrum. Meanwhile, the SEC spectrum of purified (TPAF<sub>3</sub>)<sub>3</sub> displays a feature similar to that of (TPAF<sub>5</sub>)<sub>3</sub>, but with a slightly wider peak with a  $M_w/M_n$  of 1.03. This result shows that the desired compound can be obtained in a high purity after the crude product is purified by column chromatography. The MALDI-TOF mass spectra of the purified (TPAF<sub>3</sub>)<sub>3</sub> and (TPAF<sub>5</sub>)<sub>3</sub> in Figure 2 have a single peak at 3593.5  $m/z$  for (TPAF<sub>3</sub>)<sub>3</sub> and one at 5923.8  $m/z$  for (TPAF<sub>5</sub>)<sub>3</sub>. They agree well with the structures of the respective macrocyclic trimers.

On the other hand, the impurities with linear structures should contain a fluorene moiety at the chain end. In the presence of methylsulfonic acid in the mesitylene solution, this group will be converted to a fluorene cation, which has a deep blue color in the solution. Therefore, the purity of the cyclic oligomers was also verified using a simple color test, where several drops of methylsulfonic acid were added into the mesitylene solution of the purified (TPAF<sub>3</sub>)<sub>3</sub> or (TPAF<sub>5</sub>)<sub>3</sub>. No color change was observed in both solutions, confirming that there is no residual fluorene in the purified macrocyclics.

The structures of the purified macrocyclics were also identified by FT-IR and NMR. The infrared spectra of the monomers (TPAF<sub>3</sub> and TPAF<sub>5</sub>) and the resulting macrocyclic trimers ((TPAF<sub>3</sub>)<sub>3</sub> and (TPAF<sub>5</sub>)<sub>3</sub>) are compared in Figure 3. Both monomers have peaks in the spectral range from 3598 to 3537  $cm^{-1}$ , attributed to OH stretching, which is lacking in the macrocyclics. The peak at 694  $cm^{-1}$  of monosubstituted benzene (in triphenylamine unit) found in the monomers is not present in the macrocyclics either. This result indicates that the OH group in the fluorene unit and the monosubstituted phenyl group in the triphenylamine unit have been converted after the reaction. In the <sup>1</sup>H NMR spectra of the monomer, TPAF<sub>3</sub> in Figure 4, the peaks at 2.27 ppm (singlet) and 2.01 ppm (multiplet) are due to the resonance of the CH<sub>3</sub> group on the triphenylamine unit and

the methylene protons of the octyl group adjacent to C-9 of the fluorene unit, respectively. The peaks at 7.14–7.21 ppm (multiplet) and 6.93 ppm (triplet) can be assigned to proton 6 and the proton 7 (the proton at the para position of nitrogen). Other characteristic peaks (such as protons 8–10) are also assigned. After the self-condensation reaction, the characteristic peak of the proton 7 disappears in the spectrum of (TPAF<sub>3</sub>)<sub>3</sub> and the peak at 7.14–7.21 ppm attributable to proton 6 moves to lower field. Meanwhile, the spectra in Figure 5 show similar changes upon cyclization of TPAF<sub>5</sub>. All these results demonstrate the formation of the C–C bond between the *p*-carbon of the triphenylamine unit and the C-9 of the central fluorene.

**Thermal Properties.** (TPAF<sub>3</sub>)<sub>3</sub> and (TPAF<sub>5</sub>)<sub>3</sub> were characterized by differential scanning calorimetry (DSC) (Figure 6) and thermal gravimetric analysis (TGA), and the results are summarized in Table 1. For comparison purposes, the thermal properties of poly(9,9-dioctylfluorene) (POF) were also measured and are included in Table 1. To eliminate the influence of thermal history on the results, DSC curves of both macrocyclic oligomers were taken from the second scan after the sample had been cooled from 140 °C at about 5 °C/min. The DSC curve of (TPAF<sub>3</sub>)<sub>3</sub> shows a crystallizing peak at around 167 °C followed by a melting peak at about 188 °C. The exothermic for the crystallization and the endothermic for the melting are almost the same (11.0 vs 10.8 J/g), indicating no crystalline structure in the as-prepared sample. This result suggests that this macrocyclic oligomer did not crystallize when the sample was dried from its solution; consequently, a stable amorphous structure can be expected in the (TPAF<sub>3</sub>)<sub>3</sub> films prepared from spin-coating processes and the film will remain amorphous at temperatures below 150 °C. The DSC curve of (TPAF<sub>5</sub>)<sub>3</sub> reveals an even more stable amorphous structure. No transition related to crystallization is present in the DSC curve, which shows only a broad glass transition at around 34 °C in a temperature range from -50 to 250 °C. In contrast, POF displays a high crystallization tendency. It forms crystal at a low temperature (113 °C). This result indicates that the introduction of the macrocyclic structures into the oligomers indeed effectively prevents the close packing of the molecules. TGA analysis shows that both macrocyclics are thermally stable with 5% weight loss at temperatures around 400 °C (Table 1).

**Photophysical Properties.** UV–vis absorption and photoluminescence (PL) spectra of the solution and film samples of (TPAF<sub>3</sub>)<sub>3</sub> and (TPAF<sub>5</sub>)<sub>3</sub> were measured, and the thermal stability of the PL spectra of the films were also studied by annealing the spin-coated (TPAF<sub>3</sub>)<sub>3</sub> and (TPAF<sub>5</sub>)<sub>3</sub> films on quartz slides in a vacuum at 100 °C for 24 h. The result is shown in Figure 7 and is compared with spin-coated POF films. A broad strong absorption band is observed in the solution spectrum with an absorption maximum and an absorption edge at 337.5 and 394.0 nm for (TPAF<sub>3</sub>)<sub>3</sub> and 363.8 and 414.5 nm for (TPAF<sub>5</sub>)<sub>3</sub>, showing a red-shift of



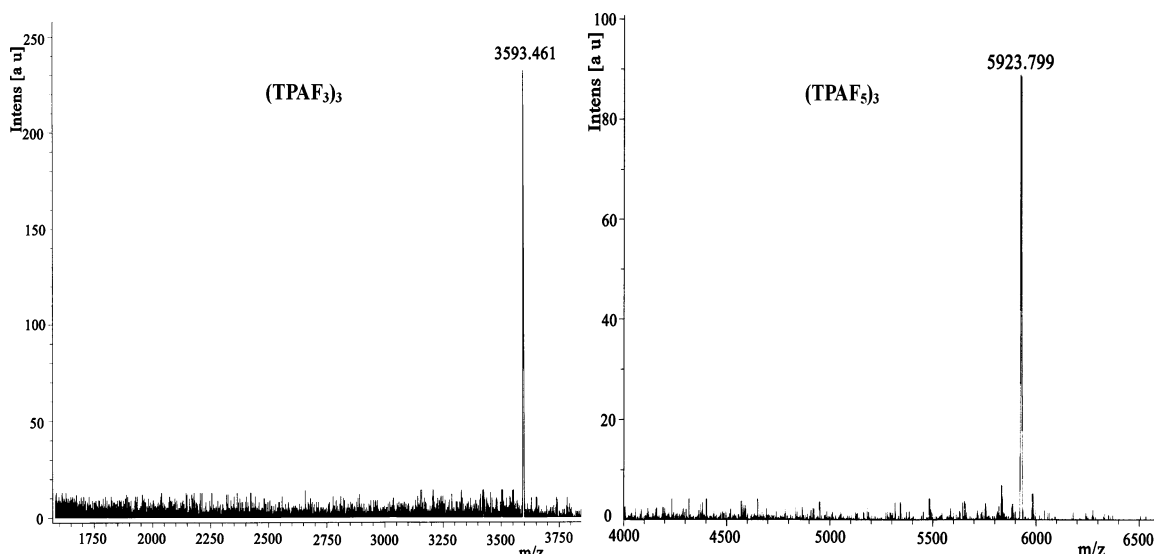


Figure 2. MALDI-TOF mass spectra of (TPAF<sub>3</sub>)<sub>3</sub> and (TPAF<sub>5</sub>)<sub>3</sub>.

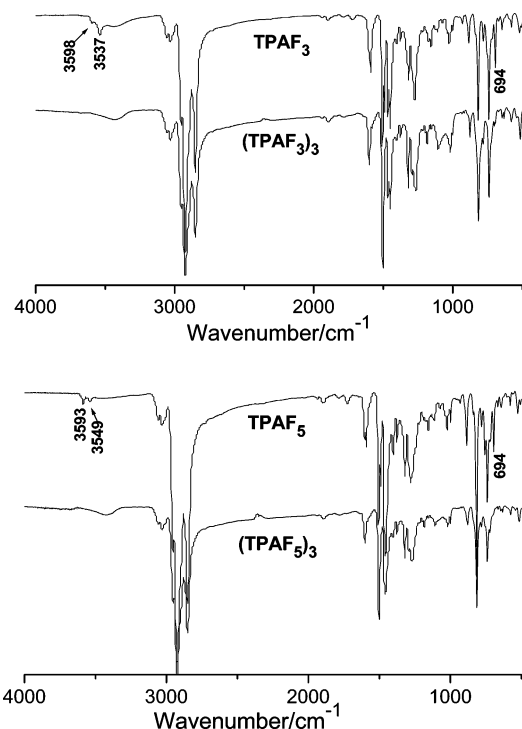


Figure 3. FTIR spectra of TPAF<sub>3</sub>, TPAF<sub>5</sub> and (TPAF<sub>3</sub>)<sub>3</sub>, (TPAF<sub>5</sub>)<sub>3</sub>.

the absorption band with the increase in the conjugation length of the oligofluorene arms. A similar trend is also present in the PL emission spectra of these two macrocyclics. In addition, there is a negligible shift in absorption spectra for both macrocyclics from solution to the solid state, indicating the absence of strong interchain interaction in the solid thin films. Both materials have very strong fluorescence in the pure-blue region. The solid-state PL quantum efficiencies of (TPAF<sub>3</sub>)<sub>3</sub> and (TPAF<sub>5</sub>)<sub>3</sub> were measured in an integrating sphere according to a literature procedure<sup>11</sup> and found to be about 57 and 52%, respectively. One striking property of these two macrocyclics is that their PL spectra

are remarkably stable upon annealing, showing very little change after annealing in a vacuum at 100 °C for 24 h (see Figure 7). Only small relative intensity changes were observed in the vibronic peaks, whereas the emission peak positions remain unchanged. The PL efficiencies of (TPAF<sub>3</sub>)<sub>3</sub> and (TPAF<sub>5</sub>)<sub>3</sub> after thermal annealing were slightly increased to 63 and 56%, respectively. On the contrary, the PL spectrum of a POF film annealed under the same condition shows a pronounced red shift of 11 nm and exhibits an additional peak at 525 nm. Because the annealing experiment was conducted under a vacuum in the dark, no thermal and photo oxidation were expected to occur. The change in the PL spectra of POF upon annealing is attributed to the formation of interchain aggregates or excimers due to the highly crystalline nature of POF.

**Cyclic Voltammetry Properties.** Cyclic voltammetry (CV) was used to investigate the ionization potential ( $E_{\text{HOMO}}$ ), the electron affinity ( $E_{\text{LUMO}}$ ), and the electrochemical stability of (TPAF<sub>3</sub>)<sub>3</sub> and (TPAF<sub>5</sub>)<sub>3</sub>. The measurement was performed in a 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub> solution in acetonitrile under argon at room temperature. The CV curves were referenced to an Ag quasi-reference electrode, which was calibrated using an internal standard, ferrocene/ferrocenium redox couple (0.35 V vs Ag/AgCl). According to de Leeuw et al.,<sup>12</sup> the ionization potential ( $E_{\text{LUMO}}$ ) and electron affinity ( $E_{\text{HOMO}}$ ) of a material are approximately equal to the onset oxidation potential (vs SCE) and the onset reduction potential (vs SCE) plus 4.4 eV (the SCE energy level below the vacuum level), respectively. The potential of the Ag quasi-reference electrode used in this experiment was determined to be −0.02 V vs SCE. Therefore, the LUMO and HOMO energy levels of the materials can be estimated using the equations  $E_{\text{HOMO}} = -(E_p' + 4.38)$  eV and  $E_{\text{LUMO}} = -(E_n' + 4.38)$  eV, respectively, where  $E_p'$  and  $E_n'$  are the onset potentials for oxidation and reduction relative to the Ag quasi-reference electrode.

The thin films of (TPAF<sub>3</sub>)<sub>3</sub> and (TPAF<sub>5</sub>)<sub>3</sub> have typical CV curves similar to those reported previously for fluorene polymers.<sup>13</sup> Both the cathode and anode scans are reversible and have similar values of onset oxidation potential ( $E_p'$ )

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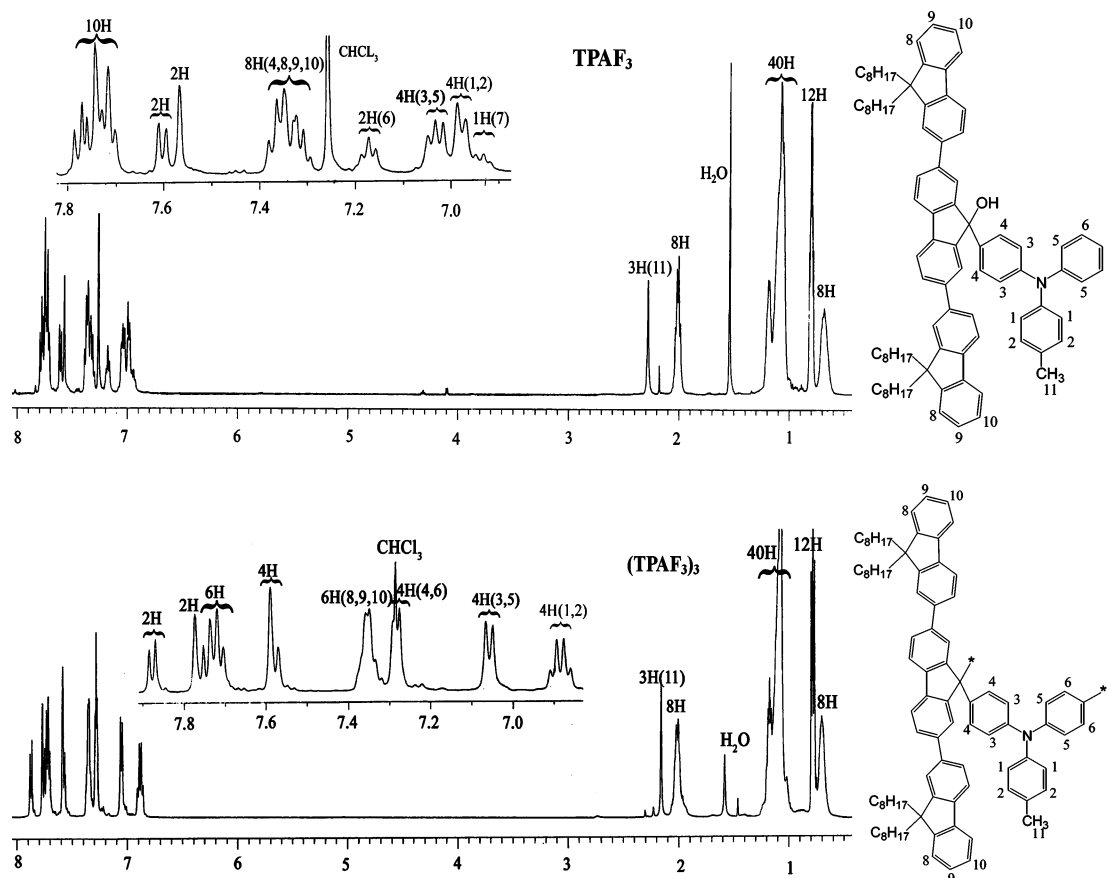


Figure 4.  $^1\text{H}$  spectra of  $\text{TPAF}_3$  and  $(\text{TPAF}_3)_3$ .

and onset reduction potential ( $E_n'$ ) for both macrocyclics, which are 0.65 and  $-2.12$  V for  $(\text{TPAF}_3)_3$  and  $0.68$  V and  $-2.10$  V for  $(\text{TPAF}_5)_3$ , respectively. These values correspond to an  $E_{\text{HOMO}}$  of  $-5.03$  eV and an  $E_{\text{LUMO}}$  of  $-2.26$  eV for  $(\text{TPAF}_3)_3$ , and an  $E_{\text{HOMO}}$  of  $-5.06$  eV and an  $E_{\text{LUMO}}$  of  $-2.28$  eV for  $(\text{TPAF}_5)_3$  (see Table 2). These data indicate that the energy barrier for hole-injection from the ITO anode ( $W_{\text{ITO}} = -4.8$  eV) to these macrocyclics are significantly lower than that to the fluorene homopolymer.<sup>13</sup> This property is attributed to the existence of the cyclic triphenylamine-based core in  $(\text{TPAF}_3)_3$  and  $(\text{TPAF}_5)_3$ . Traditionally, introduction of triphenylamine units in conjugated polymers or organic molecules was found to effectively enhance the hole-injecting properties of the resulting materials.<sup>14</sup> At the same time, it also causes an increase in the LUMO energy level, resulting in an increased energy barrier for electron injection from the metal cathode. For example, introducing triphenylamine units into a polyfluorene main chain makes the LOMO level about 0.2 eV higher than POF.<sup>13a,b</sup> The existence of the triphenylamine units in these macrocyclics does not apparently show this effect; the LUMO energy levels of both

oligomers are about  $-2.28$  eV, comparable to that of the fluorene homopolymer.<sup>13c</sup> This result indicates that introducing a triphenylamine macrocyclic core into these oligomers promotes their hole-injection capability, but does not sacrifice their electron-injection capability. This property should be attributed to the novel structure of the multi-triphenylamine cyclic core, which is not conjugated with the oligofluorene units in the oligomers. This property is superior for balancing the hole and electron injection into the emitting layers. Figure 8 also shows that both p-doping and n-doping processes of  $(\text{TPAF}_3)_3$  and  $(\text{TPAF}_5)_3$  are reversible, indicating a high stability for both hole and electron injection. Under successive multiple potential scans as shown in Figure 8,  $(\text{TPAF}_5)_3$  film demonstrates an extraordinarily high stability, with the CV curves remaining unchanged in 10 scans. However,  $(\text{TPAF}_3)_3$  has a relatively poor stability under the multiple CV scans. About 10% loss in intensity occurs after each scan.

**Electroluminescence (EL) Properties.** It is well-known that there exists a significant energy barrier for hole injecting from the ITO anode to POF, because the polymer has a low-lying HOMO energy level at  $-5.63$  eV. As a result, an additional hole-injection/transport layer, such as PEDOT-PSS, is necessary in polyfluorene-based PLED structures to achieve acceptable device performance.<sup>15</sup> However, PEDOT-PSS is not perfect because of its significant absorption in the visible region and its unstable interface with ITO.<sup>16</sup>

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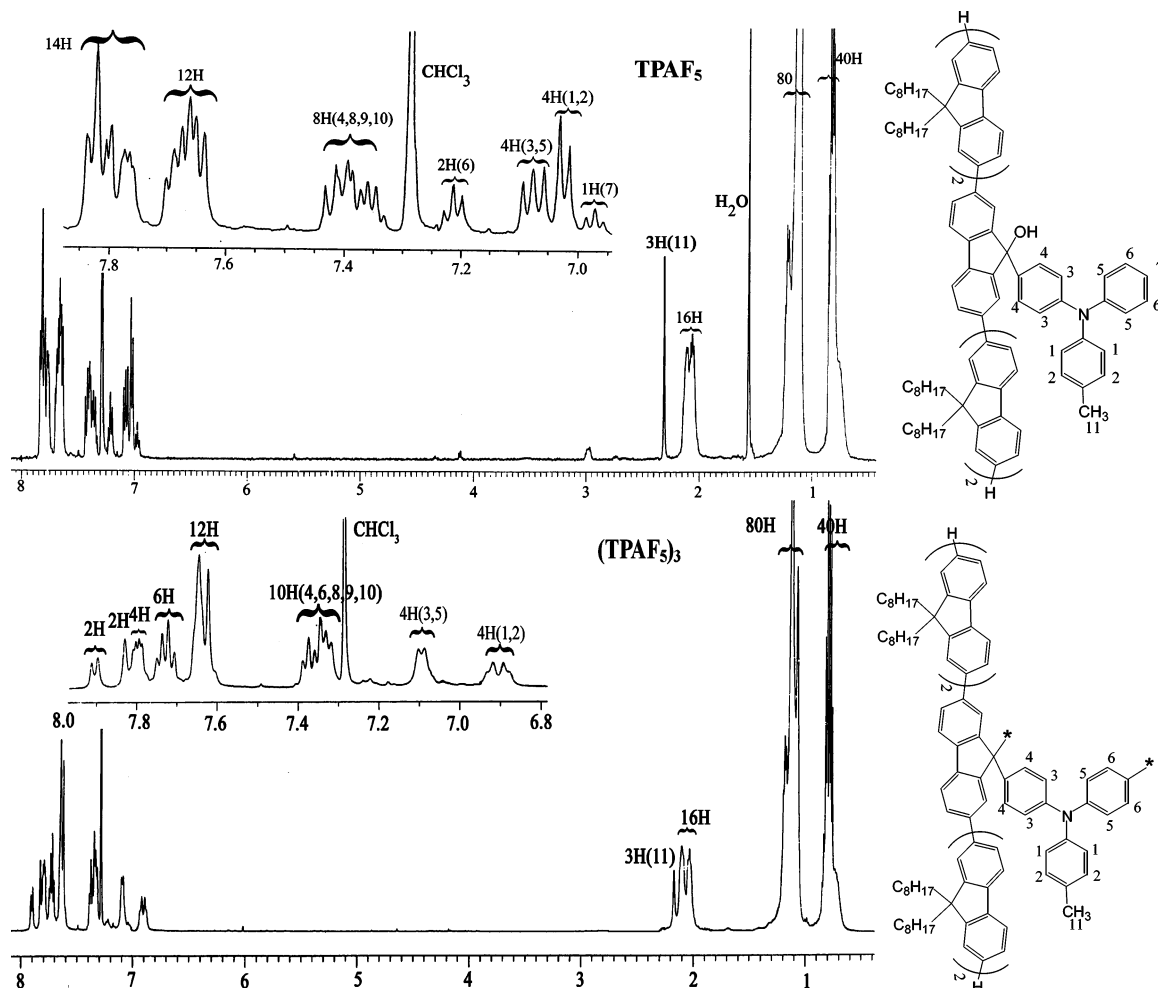


Figure 5.  $^1\text{H}$  spectra of  $\text{TPAF}_5$  and  $(\text{TPAF}_5)_3$ .

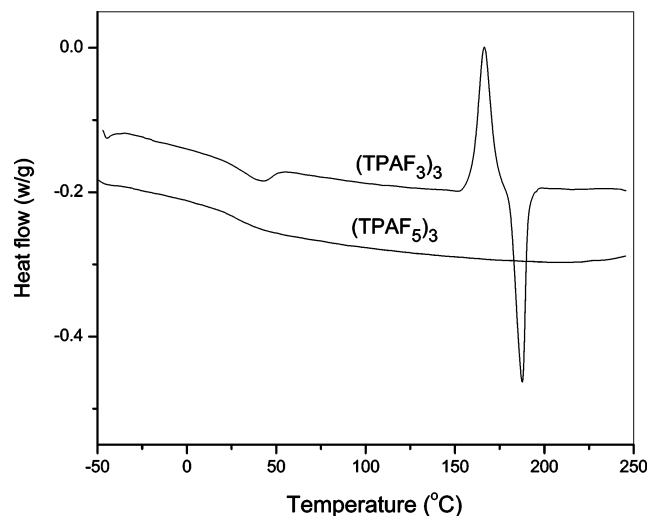
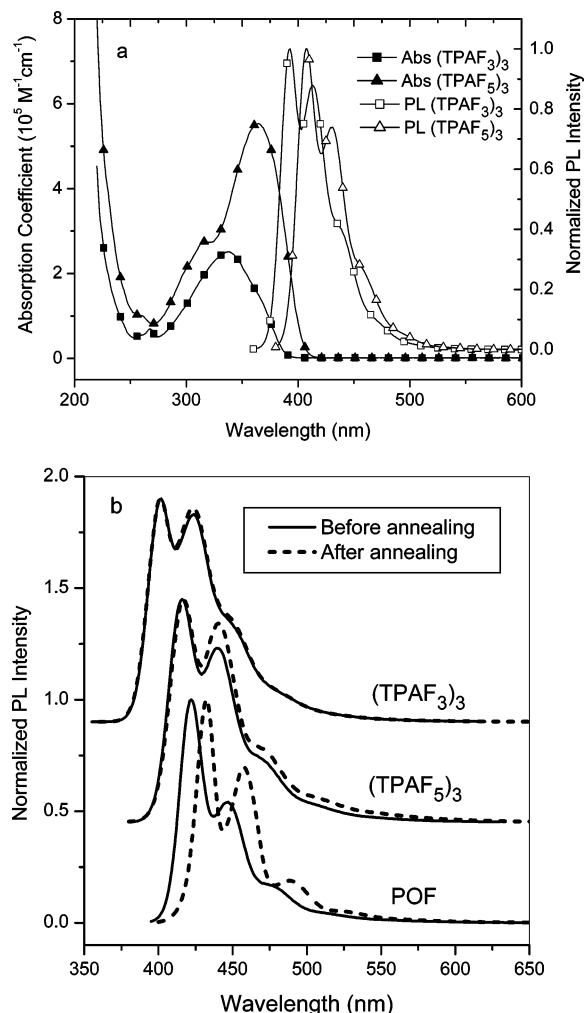


Figure 6. DSC curves of  $(\text{TPAF}_3)_3$  and  $(\text{TPAF}_5)_3$  in nitrogen at a heating rate of  $10\text{ }^\circ\text{C}/\text{min}$ .

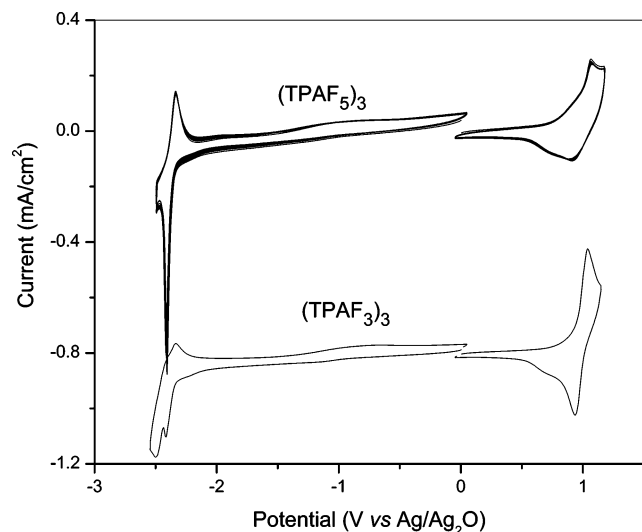
Because both  $(\text{TPAF}_3)_3$  and  $(\text{TPAF}_5)_3$  have high-lying HOMO energy levels, they might be able to act as a hole-injection layer so that PEDOT-PSS could be eliminated from the device. Thus, multilayer devices with a configuration of ITO/ $(\text{TPAF}_3)_3$  or  $(\text{TPAF}_5)_3$ /TPBI/LiF/Al were fabricated to investigate the EL properties of  $(\text{TPAF}_3)_3$  and  $(\text{TPAF}_5)_3$ . In these devices,  $(\text{TPAF}_3)_3$  and  $(\text{TPAF}_5)_3$  act as a hole-transporting emitting layer, and TPBI has a wide band gap

and functions as a hole-blocking/electron-transporting layer. In the previous studies, Heeger's group and our group independently demonstrated that inserting a hole-blocking layer between the fluorene-based emissive layer and the cathode provides improved blue-emission stability.<sup>17</sup> In addition, this hole-blocking layer can also protect the emissive layer from damage during cathode deposition.<sup>17a</sup> As can be seen from Figure 9, at low voltages, these macrocyclics have deep blue EL with almost negligible emission in the 500–600 nm region. The CIE 1931 chromaticity coordinates of the emission of  $(\text{TPAF}_3)_3$  and  $(\text{TPAF}_5)_3$  are (0.176, 0.066) and (0.164, 0.076), respectively, at about 6 V. These values are very close to the National Television System Committee (NTSC) standard for blue emission (0.14, 0.08). Although low-energy emission bands appear in  $(\text{TPAF}_3)_3$  at high voltages, the EL emission remains well in the blue region. For comparison purposes, POF was also tested as an emissive layer in the same device structure. Figure 9 shows that the EL color stability of  $(\text{TPAF}_5)_3$  is better than that of POF. The EL spectrum of this material shows almost no change when the driving voltage increases from 6 to 12 V, whereas  $(\text{TPAF}_3)_3$  has an EL color stability similar to that of POF, with an appearance of a weak broad

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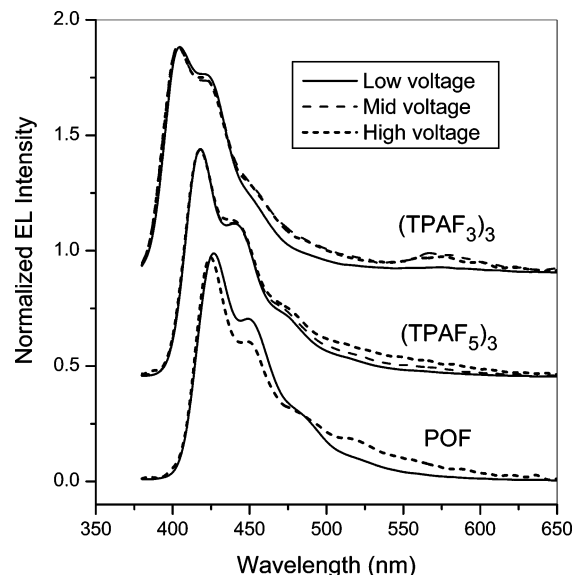
**Figure 7.** (a) UV-vis absorption and PL spectra of (TPAF<sub>3</sub>)<sub>3</sub> and (TPAF<sub>5</sub>)<sub>3</sub> in hexanes; (b) Thin film PL spectra of (TPAF<sub>3</sub>)<sub>3</sub>, (TPAF<sub>5</sub>)<sub>3</sub>, and POF before and after thermal annealing.



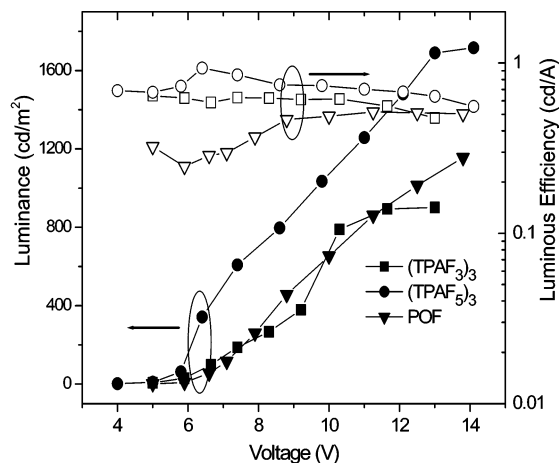
**Figure 8.** CV curves of (TPAF<sub>3</sub>)<sub>3</sub> and (TPAF<sub>5</sub>)<sub>3</sub> (10 successive scans) for both n-doping and p-doping processes.

band around 550 nm at high voltages. The slightly poor stability of (TPAF<sub>3</sub>)<sub>3</sub> may be related to its crystallization tendency.

Figure 10 illustrates the luminance-voltage (*L-V*) and luminous efficiency-voltage (*LE-V*) characteristics of the



**Figure 9.** Electroluminescence spectra of (TPAF<sub>3</sub>)<sub>3</sub>, (TPAF<sub>5</sub>)<sub>3</sub>, and POF at different voltages, with the films thickness of 80 nm in devices and a configuration of ITO/polymer/TPBI/LiF/Al. The resulting CIE 1931 chromaticity coordinates of the emission at low, middle, and high voltages are (0.176, 0.066)/6.0 V, (0.194, 0.110)/10.3 V, (0.199, 0.117)/13.0 V for (TPAF<sub>3</sub>)<sub>3</sub>; (0.164, 0.076)/6.0 V, (0.176, 0.096)/12.0 V, (0.181, 0.123)/14.0 V for (TPAF<sub>5</sub>)<sub>3</sub>; and (0.159, 0.081)/6.5 V, (0.178, 0.136)/14.0 V for POF.



**Figure 10.** Luminance-voltage (*L-V*) and luminous efficiency-voltage (*LE-V*) characteristics of (TPAF<sub>3</sub>)<sub>3</sub>- and (TPAF<sub>5</sub>)<sub>3</sub>-based devices.

device from (TPAF<sub>3</sub>)<sub>3</sub>, (TPAF<sub>5</sub>)<sub>3</sub>, and POF. As anticipated, (TPAF<sub>3</sub>)<sub>3</sub> (5 V) and (TPAF<sub>5</sub>)<sub>3</sub> (4 V) exhibit lower turn-on voltages than POF (6 V) because of their lower hole injection barriers. Because the triphenylamine units are incorporated with oligofluorenes in (TPAF<sub>3</sub>)<sub>3</sub> and (TPAF<sub>5</sub>)<sub>3</sub> in a nonconjugated manner, the introduction of triphenylamine units brings the HOMO energy level of the macrocyclics close to the work function of ITO, while it has not had an apparent influence on their LUMO energy level as discussed above. This effect makes the electron and hole injection into the macrocyclic emitting layer more balanced than into POF and may account for the higher luminance and luminous efficiency for the macrocyclic-based devices, as shown in Figure 10. The best device performance was obtained using (TPAF<sub>5</sub>)<sub>3</sub> as the emitting layer with a maximum luminance of 1716 cd/m<sup>2</sup> at 14.1 V and a peak luminous efficiency of 0.93 cd/A at 340 cd/m<sup>2</sup>. These values are comparable to the



literature data for solution-processed blue-light-emitting devices.<sup>9a,18</sup>

## Conclusion

Novel triphenylamine-functionalized macrocyclic oligofluorenes (TPAF<sub>3</sub>)<sub>3</sub> and (TPAF<sub>5</sub>)<sub>3</sub> were synthesized using a simple Friedel–Craft reaction. The triphenylamine-based cyclic core serves as a nonconjugated spacer bearing oligofluorene arms to form a multi-H shaped structure of the oligomers so that the optoelectronic properties of the individual oligofluorene arm remain relatively unperturbed. Therefore, the presence of the cyclic triphenylamine-based core raises the HOMO energy levels of (TPAF<sub>3</sub>)<sub>3</sub> and (TPAF<sub>5</sub>)<sub>3</sub> but leaves their LUMO energy levels somewhat unchanged, comparable to the fluorene homopolymer. Morphologically stable amorphous (TPAF<sub>5</sub>)<sub>3</sub> films have excellent electrochemical stability for both p-doping and n-doping processes, with the CV curves in 10 successive scans remaining unchanged. Pure blue electroluminescence was obtained from either device using (TPAF<sub>3</sub>)<sub>3</sub> or (TPAF<sub>5</sub>)<sub>3</sub> as a hole-transporting emitting layer.

## Experimental Section

**Characterization.** <sup>1</sup>H NMR spectra of the materials were recorded on a 500 MHz Bruker spectrometer in CDCl<sub>3</sub>, and tetramethylsilane was used as an internal standard. IR spectra were obtained using a Nexus 870 FT-IR spectrophotometer. Molecular weight analysis was done by size-exclusion chromatography (SEC) using a Viscotek SEC system, which consisted of a Viscotek VE1122 HPLC pump coupled with a Viscotek TDA Triple detector and a Viscotek 2501 UV detector operated at 260 nm. A set of ViscoGEL columns (G4000H and G5000H) were used and calibrated using a set of polystyrene standards in tetrahydrofuran. Differential scanning calorimetric (DSC) measurements were performed on a TA Instruments DSC 2920. Thermogravimetric analysis (TGA) data were obtained using a Perkin-Elmer Thermal Analysis system. Both DSC and TGA measurements were done in a N<sub>2</sub> atmosphere at a heating rate of 10 °C/min. UV–vis absorption spectra were collected on a Hewlett-Packard 8453 spectrophotometer. Fluorescence measurements were carried out on a Spex Fluorolog 3 spectrometer using the absorption maxima of the materials as the excitation wavelengths. The PL quantum yields of the thin films of the macrocyclics spin-coated on quartz slides were measured using a commercial spectrofluorimeter combined with an integrating sphere according to the literature procedure.<sup>11</sup> Positive-ion MALDI-TOF/TOF mass spectrometry was performed using an Autoflex II TOF/TOF time-of-flight mass spectrometer (Bruker Daltonics, Germany). Briefly, 0.5 mg of sample was dissolved in 0.5 mL of dichloromethane. The sample solution (0.5 mL) was mixed with 0.05 mL of the matrix solution (50% acetonitrile with 0.5% trifluoroacetic acid solution saturated with cinnamic acid). Diluted solution (1 μL) was placed on the concave flat surfaces of a stainless steel plate and then air-dried. The spectra were obtained using reflector mode, and ions generated by a pulsed laser beam (nitrogen laser λ = 337 nm, 25 Hz) were accelerated to 19.0 kV with a delayed extraction (180 ns). The mass was analyzed by FlexAnalysis (Ver. 2.4, Bruker Daltonics, Germany).

**EL Device Fabrication and Testing.** ITO-coated glass substrates (15 Ω/square) were patterned by conventional wet-etching process using a mixture of HCl (6 N) and HNO<sub>3</sub> (0.6 N) as the etchant. The active area of each device was 5 × 6 mm<sup>2</sup>. After patterning, the substrates were rinsed in deionized water and then ultrasonicated sequentially in acetone (20 °C) and 2-propanol (65 °C). Immediately prior to device fabrication, the ITO substrate was treated in a UV-ozone oven for 15 min. Macrocyclic (TPAF<sub>3</sub>)<sub>3</sub> or (TPAF<sub>5</sub>)<sub>3</sub> was dissolved in CHCl<sub>3</sub> and then spin-coated on the treated substrate. The resulting film was about 80 nm thick, as measured by a Dektak surface profilometer. 1,3,5-Tris(*N*-phenylbenzimidazol-2-yl)-benzene (TPBI, 30 nm) was vacuum-deposited as a hole-blocking layer. Finally, LiF (1 nm) and Al (100 nm) were deposited as the cathode. The devices were tested in air under ambient conditions with no protective encapsulation. EL spectra, device luminance, and current–voltage characteristics were recorded using a combination of a Photo Research PR-650 SpectraScan and a Keithley 238 Source meter.

**Materials.** Tetrahydrofuran and diethyl ether were dried by Na and distilled prior to use. All other reagents were purchased from Alfa Aesar and used without further purification. *N*-(4-Bromophenyl)-*N*-(4-methylphenyl) aniline,<sup>19a</sup> 7-dibromo-fluorenone,<sup>19b</sup> 2-bromo-9,9-di-*n*-octylfluorene and 2,7-dibromo-9,9-di-*n*-octylfluorene,<sup>19c</sup> and 9,9-di-*n*-octylfluorenyl-2-boronic acid and 9,9,9',9'-tetra-*n*-octyl-2,2'-bifluorenyl-7-boronic acid<sup>19d</sup> were prepared according to the literature procedures.

**TPAF-Br<sub>2</sub>.** To a solution of *N*-(4-bromophenyl)-*N*-(4-methylphenyl) aniline (4.06 g, 12 mmol) in anhydrous tetrahydrofuran (30 mL) was slowly added *n*-BuLi (2.5 M in *n*-hexane, 6.7 mL, 12.6 mmol) at –78 °C, where the reaction mixture was stirred for 1 h before the addition of 2,7-dibromofluorenone (4.06 g, 12 mmol) in 40 mL of tetrahydrofuran. The solution was then freely warmed to room temperature and stirred overnight followed by quenching with 30 mL of water. The aqueous layer was extracted with ethylether for three times. The combined organic layer was washed with brine before drying over anhydrous MgSO<sub>4</sub>. The crude product was collected by evaporating off the solvent and was then purified by column chromatography on silica gel to afford TPAF-Br<sub>2</sub> as a yellow solid, mp 108–110 °C (4.13 g, 59%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.50–7.53 (m, 6H), 7.22–7.28 (m, 2H), 7.18 (d, *J* = 8 Hz, 2H), 7.06–7.13 (m, 4H), 6.99–7.04 (m, 3H), 6.95 (d, *J* = 10 Hz, 2H), 2.34 (s, 3H). FT-IR (λ, cm<sup>–1</sup>): 3524, 3054, 3026, 2953, 2921, 2853, 1591, 1506, 1491, 1447, 1411, 1318, 1274, 1161, 1061, 877, 812, 754, 698, 677, 526, 470.

**General Procedure for the Preparation of the Monomers TPAF<sub>3</sub> and TPAF<sub>5</sub> via the Suzuki Coupling Reaction.** Into a mixture of 20 mL of toluene and 15 mL of 2.0 M aqueous solution of Na<sub>2</sub>CO<sub>3</sub> in a 100 mL flask were added TPAF-Br<sub>2</sub> (1 uiv.), 9,9-di-*n*-octylfluorenyl-2-boronic acid (2.2 equiv.), or 9,9,9',9'-tetra-*n*-octyl-2,2'-bifluorenyl-7-boronic acid (2.2 equiv.) and tripropylmethylammonium chloride (20% by weight of the monomer). The mixture was evacuated under a vacuum and filled with nitrogen three times; Pd(PPh<sub>3</sub>)<sub>4</sub> (0.005 equiv.) was then added under the protection of nitrogen. The reaction mixture was stirred under refluxing for 24 h. The organic layer was then separated and washed with brine, dried over anhydrous MgSO<sub>4</sub>, and concentrated by evaporating off the solvent for further purification by column chromatography on silica gel.

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**TPAF<sub>3</sub>**. Pale yellow solid: mp 97–99 °C (1.46 g, 72%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): 7.70–7.78 (m, 10H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.57 (s, 2H), 7.29–7.38 (m, 8H), 7.14–7.20 (m, 2H), 7.01–7.07 (m, 4H), 6.96–6.99 (m, 4H), 6.93 (t, *J* = 6.5 Hz, 1H), 2.27 (s, 3H), 1.98–2.03 (m, 8H), 0.98–1.18 (m, 40H), 0.77–0.84 (m, 12H), 0.60–0.73 (m, 8H). FT-IR ( $\lambda$ , cm<sup>-1</sup>): 3598, 3537, 3059, 3033, 2952, 2925, 2852, 1593, 1507, 1492, 1465, 1449, 1318, 1275, 1155, 1026, 885, 818, 741, 694, 520. MS (AutoflexTOF/TOF): *m/z* 1215.8.

**TPAF<sub>5</sub>**. Pale yellow solid: mp 142–144 °C (3.23 g, 81%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.75–7.83 (m, 14H), 7.63–7.72 (m, 12H), 7.34–7.43 (m, 8H), 7.18–7.23 (m, 2H), 7.04–7.09 (m, 4H), 6.99–7.03 (m, 4H), 6.97 (t, *J* = 7.0 Hz, 1H), 2.26 (s, 3H), 2.0–2.15 (m, 16H), 1.05–1.25 (m, 80H), 0.65–0.86 (m, 40H). FT-IR ( $\lambda$ , cm<sup>-1</sup>): 3593, 3549, 3058, 3032, 2953, 2925, 2852, 1592, 1506, 1492, 1459, 1319, 1280, 1154, 1023, 885, 814, 739, 694, 525. MS (AutoflexTOF/TOF): *m/z* 1992.5.

**General Procedure for the Preparation of (TPAF<sub>3</sub>)<sub>3</sub> and (TPAF<sub>5</sub>)<sub>3</sub>**. In a 250 mL flask, TPAF<sub>3</sub> or TPAF<sub>5</sub> (1 g) was dissolved in 100 mL of mesitylene, and two drops of methylsulfonic acid were added. The reaction mixture was stirred at 80 °C for 3 h under the protection of N<sub>2</sub> and was then dried over anhydrous MgSO<sub>4</sub> and concentrated by evaporating off the solvent for further purification by column chromatography on silica gel using dichloromethane/petroleum ether (1/4, v/v for (TPAF<sub>3</sub>)<sub>3</sub> and 1/5, v/v for (TPAF<sub>5</sub>)<sub>3</sub>) as eluents.

**(TPAF<sub>3</sub>)<sub>3</sub>**. Pale yellow powder (0.72 g, 71%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.87 (d, *J* = 7.8 Hz, 2H), 7.70–7.77 (m, 8H), 7.56–7.59 (m, 4H), 7.31–7.38 (m, 6H), 7.26–7.29 (m, 4H), 7.05 (d, *J* = 8.4 Hz, 4H), 6.84–6.93 (m, 4H), 2.16 (s, 3H), 1.90–2.05-

(m, 8H), 1.00–1.22 (m, 40H), 0.75–0.8 (m, 12H), 0.62–0.75 (m, 8H). <sup>13</sup>C NMR (100 MHz in CD<sub>2</sub>Cl<sub>2</sub>, solvent peak at 53.80 ppm as reference):  $\delta$  153.27, 151.82, 151.40, 147.21, 145.04, 141.71, 141.06, 140.89, 140.35, 139.72, 139.13, 133.60, 130.11, 129.33, 129.12, 127.44, 127.15, 126.38, 125.86, 124.91, 123.37, 123.33, 121.85, 120.84, 120.19, 120.04, 65.31, 55.55, 40.66, 32.10, 29.55, 29.54, 24.18, 22.94, 14.22. MS (AutoflexTOF/TOF): *m/z* 3593.5.

**(TPAF<sub>5</sub>)<sub>3</sub>**. Pale yellow powder (0.68 g, 68%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.90 (d, *J* = 7.8 Hz, 2H), 7.77–7.85 (m, 6H), 7.69–7.77 (m, 6H), 7.60–7.66 (m, 12H), 7.30–7.39 (m, 10H), 7.09 (d, *J* = 7.8 Hz, 4H), 6.85–6.95 (m, 4H), 2.17 (s, 3H), 1.95–2.12 (m, 16H), 1.03–1.22 (m, 80H), 0.65–0.88 (m, 40H). <sup>13</sup>C NMR (100 MHz in CD<sub>2</sub>Cl<sub>2</sub>, solvent peak at 53.80 ppm as reference):  $\delta$  153.21, 152.20, 152.17, 151.85, 151.40, 147.28, 145.07, 141.71, 141.17, 140.94, 140.77, 140.74, 140.64, 140.35, 140.29, 139.77, 139.18, 133.64, 130.14, 129.38, 127.38, 127.23, 127.15, 126.48, 126.36, 125.87, 124.90, 123.45, 123.32, 121.94, 121.79, 121.73, 120.90, 120.36, 120.27, 120.06, 65.41, (55.74, 55.58), (40.74, 40.69), 32.16, 32.12, (30.37, 30.35), (29.58, 29.56), 24.29, 24.23, (22.97, 22.96), 14.23. MS (AutoflexTOF/TOF): *m/z* 5923.8.

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