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3D Monodisperse Oligofluorenes with Non-Conjugated Triphenylamine-Based Cores: Synthesis and Optoelectronic Properties

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Two 3D monodisperse oligofluorenes with non-conjugated triphenylamine-based cores have been synthesized by Friedel–Crafts copolycondensation reaction. The oligomers, PF_3-TPA and PF_3-TPA_3, consist of three fluorene pentamer arms that are connected non-conjugately through a triphenylamine (TPA) and 1,3,5-tris(triphenylamino)benzene core (TPA_3), respectively, at the 9-position of the central fluorene of the pentafluorene arms. The coplanar structures of the cores and the linkages at the centre of the pentafluorene arms produced a 3D structure of oligomers. This specific structure efficiently retarded the crystallization tendencies of the pentafluorene arms and gave the materials completely amorphous morphological structures. Both oligomers emit deep-blue fluorescence with high efficiencies in thin films ($\phi_{\text{pl-film}}$ = 67 % for PF_3-TPA_3 and 86 % for PF_3-TPA). The introduction of triphenylamine units into the core promoted the hole-injection ability while not obviously scarificing the electron-injection ability of the oligomers. The multi-layer devices ITO/PEDOT-PSS/PF_3-TPA_3 and PF_3-TPA/TPBI/LiF/Al were fabricated to investigate the electroluminescence (EL) properties of the two oligomers. Both oligomers showed a low turn-on voltage of 4 V. The luminances reached 1946 cd/m^2 at 7.5 V in the PF_3-TPA_3 device and 1055 cd/m^2 at 8 V in the PF_3-TPA device. The EL efficiencies at this luminance were 1.63 and 1.57 cd/A, respectively.

Introduction

In the past decade, fluorene-based conjugated polymers have emerged as a very promising class of blue-light-emitting materials for use in polymer light-emitting diodes (PLEDs) because of their high photoluminescence (PL) and electroluminescence (EL) quantum efficiencies, thermal stability, good solubility and facile functionalization at the 9-position of fluorene.[1] However, the application of polyfluorenes in PLEDs has been hampered by the formation of an emission tail at long wavelengths during device operation due to undesired chain aggregation, excimer formation and keto defects.[2] Some researchers have demonstrated that the introduction of bulky groups at the 9-position of fluorene or introduction of cross-linkable moieties tended to suppress this emission and to improve the thermal stability of the PL spectra.[3] Another challenge is how to achieve balanced charge injection and mobility in fluorene oligomers/polymers. One of the approaches used to address this issue is to modify the chemical structures of the polyfluorenes by copolymerization with dibenzothiophene *S*,*S*-dioxide,[4] carbazole[5] or triphenylamine.[6] The introduction of electron-donating units into conjugated polyfluorene can effectively enhance the hole-injecting properties of the resulting materials. However, at the same time, it also causes an increase in the LUMO energy level, which results in an increased energy barrier for electron injection from the metal cathode. For example, introducing triphenylamine units into a polyfluorene main chain raises the LUMO level by about 0.2 eV relative to the parent polymer.[5a,7] To promote hole-injection capability in the polyfluorene without sacrificing its electron-injection capability, researchers recently directed their attention towards triphenylamine-substituted polyfluorene derivatives[8] and found that the introduction of triphenylamine groups at the 9-position of the fluorene simultaneously has the advantages of 1) higher solubility, 2) reduced interchain interaction and 3) improved hole injection. This non-conjugated connection between the triphenylamine and fluorene is advantageous for balancing hole and electron injection into emitting layers.

On the other hand, monodisperse oligofluorenes have recently become the subject of intense study for their optoelectronic applications[9] due to their well-defined conjugation lengths and molecular structures, ease of purification and characterization, and solution processing. Moreover,

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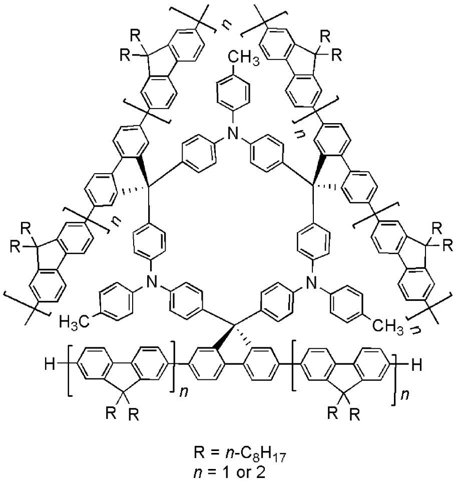
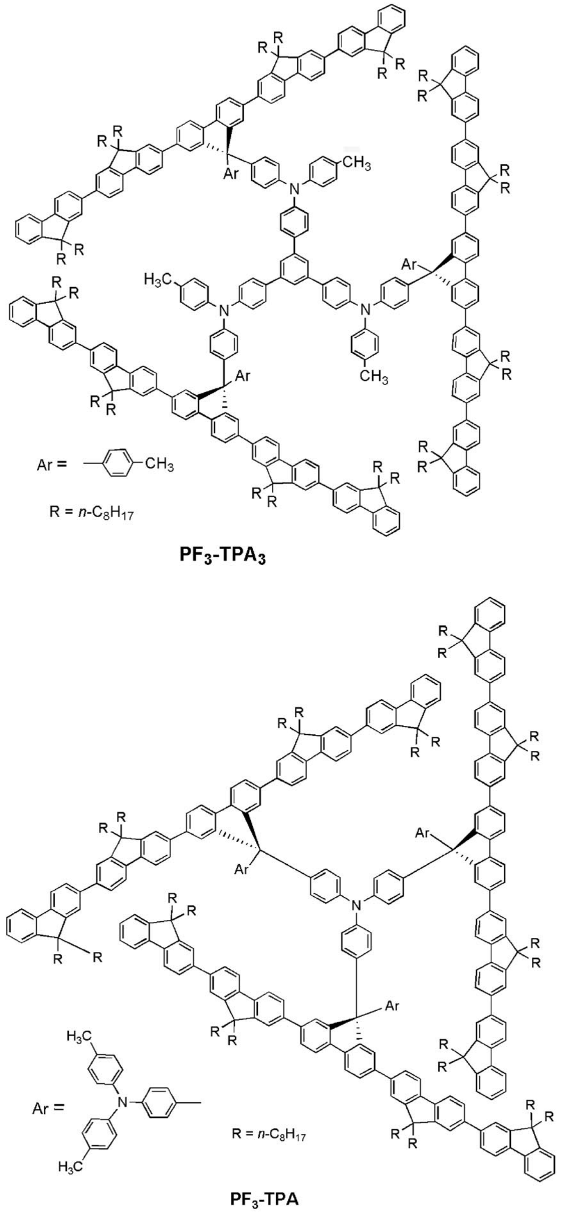
recent rapid development of new synthetic methodologies has made it possible to design a variety of monodisperse oligomers, permitting efficient colour and energy-level tuning by the control of effective conjugation length as well as by the introduction of electron-donating and -withdrawing moieties into the conjugated systems. For example, Cao and co-workers synthesized extended π-conjugated dendrimers and star-shaped molecules,[9e,9f] Lai et al. synthesized six-arm triazatruxenes,[9a] Liu et al. reported a series of Si-based tetrahedral luminescent materials,[9g] Shih et al. designed and synthesized a series of carbazole/fluorene hybrids[9h] and Huang and co-workers synthesized a novel series of monodisperse starburst macromolecular materials based on fluorene.[9k]

Inspired by these results, we recently synthesized monodisperse triphenylamine-substituted oligofluorenes[10] (shown in Scheme 1) in which the triphenylamine cyclic core serves as a non-conjugated spacer bearing oligofluorene arms in a multi-H shaped structure of oligomers. As a result, the optoelectronic properties of the individual oligofluorene arms remained relatively unperturbed. These cyclic oligomers were prepared by a Friedel–Crafts self-condensation reaction[10] so that oligomers of different sizes are possibly prepared. In this article we report two 3D monodisperse oligofluorenes, one with a 1,3,5-tris(triphenylamino)benzene (TPA_3) core and the other with a triphenylamine (TPA) core (shown in Scheme 2), prepared by a Friedel–Crafts copolycondensation reaction. This design gave the products well-defined structures. The coplanar structures of the TPA-based cores and the connection at the centre of the pentafluorene arms gave the oligomers a 3D steric conformation. In the products, the triphenylamine units and oligofluorenes are also non-conjugately connected at the 9-position of the fluorenes, as reported in our previous work.[10] The thermal, optical and electrochemical properties of the polymers were investigated and OLEDs from these polymers were fabricated and characterized.



Scheme 1. The structure of monodisperse triphenylamine-substituted oligofluorenes prepared by the Friedel–Crafts self-condensation reaction.



PF_3-TPA_3

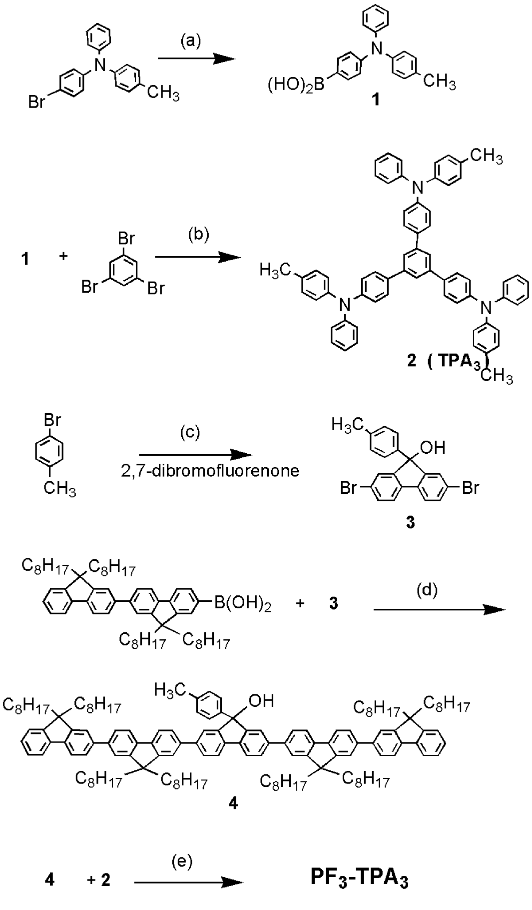
PF_3-TPA

Scheme 2. The structures of the 3D monodisperse oligofluorenes PF_3-TPA and PF_3-TPA_3 with a TPA-based core prepared by the Friedel–Crafts copolycondensation reaction.

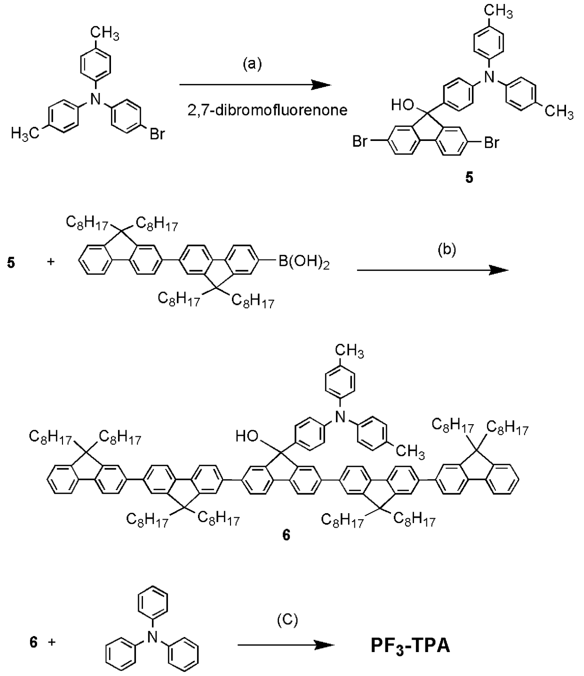
Results and Discussion

Synthesis and Characterization

The synthetic procedures used to prepare PF_3-TPA_3 and PF_3-TPA are outlined in Scheme 3 and Scheme 4 respectively. PF_3-TPA_3 was synthesized according to the reported procedure.[10] First, 1-bromo-4-methylbenzene was treated with *n*BuLi in tetrahydrofuran at –78 °C followed by the addition of 2,7-dibromofluorenone to give 2,7-dibromo-9-(*p*-tolyl)fluoren-9-ol (**3**). This compound was treated with 9,9,9′,9′-tetra-*n*-octyl-2,2′-bifluorenyl-7-boronic acid under Suzuki coupling reaction conditions in a mixture of toluene and a 2 M aqueous solution of sodium carbonate (Na_2CO_3). Tetrakis(triphenylphosphane)palladium [$(PPh_3)_4Pd^0$] was used as the catalyst and tricaprylylmethylammonium chloride (Aliquat 336) was used as the phase-transfer catalyst. The mixture was heated at reflux with stirring for 24 h to give the fluorene pentamer **4**. The 3D oligofluorene (PF_3-TPA_3) was then prepared by a copolycondensation reaction of an excess of compound **4** with compound **2** (TPA_3) in mesitylene at 80 °C for 3 h in the presence of *p*-toluenesulfonic acid. This polycondensation reaction follows the aromatic electrophilic substitution mechanism. Triphenylamine is a very reactive aromatic compound for the electrophilic substitution of fluorenol in the presence of a strong acid.[11–13] The *para* position with respect to the nitrogen is a reactive site whereas the *ortho* position has proven to be non-reactive as a result of steric hindrance.[10–12] The synthetic route used to synthesize PF_3-TPA was similar to the procedure used for PF_3-TPA_3 with (4-bromophenyl)di-*p*-tolylamine as the starting material and triphenylamine as the core. The final Friedel–Crafts reaction afforded high yields of 73% for PF_3-TPA_3 and 88% for PF_3-TPA after purification by column chromatography.



Scheme 3. Synthetic route for the preparation of the 3D monodisperse oligofluorenes with a non-conjugated TPA_3 core (PF_3-TPA_3). Reagents and conditions: (a) *n*BuLi/THF, –78 °C, 1 h, $B(OiPr)_3$, –78 °C to room temp., 10 h, 2 M HCl, room temp. 1 h; (b) [$(PPh_3)_4Pd^0$], toluene, 2 M Na_2CO_3, reflux, 24 h; (c) *n*BuLi/THF, –78 °C 1 h, 2 M HCl, room temp. 1 h; (d) [$(PPh_3)_4Pd^0$], toluene, 2 M Na_2CO_3, Aliquat 336, reflux, 24 h; (e) *p*-toluenesulfonic acid, mesitylene, 80 °C, 3 h.



Scheme 4. Synthetic route for the preparation of the steric monodisperse oligofluorene with a non-conjugated TPA core (PF_3-TPA). Reagents and conditions: (a) *n*BuLi/THF, –78 °C 1 h, 2 M HCl, room temp. 1 h; (b) [$(PPh_3)_4Pd^0$], toluene, 2 M Na_2CO_3, Aliquat 336, reflux, 24 h; (c) *p*-toluenesulfonic acid, mesitylene, 80 °C, 3 h.

The structures and monodispersities of PF_3-TPA_3 and PF_3-TPA were identified by NMR, size-exclusion chromatography (SEC) and MALDI-TOF mass spectroscopy. In the ^1H NMR spectrum of PF_3-TPA_3, the peaks at δ = 2.33 (3 H, singlet), 2.29 (3 H, singlet) and 2.05 ppm (16 H, multiplet) have been attributed to the resonance of the CH_3 groups in the tolyl moieties at the 9-position of the central fluorene units, the CH_3 groups in the TPA units and the methylene units in the octyl groups adjacent to the C-9 of the fluorene units. This result is consistent with the structure of PF_3-TPA_3 in which the three pentafluorene arms are connected to the TPA_3 core. Similar characteristic peaks have also been assigned in the ^1H NMR spectrum of PF_3-TPA. The peaks at δ = 2.29 (6 H, singlet) and 2.05 ppm (16 H, multiplet) are due to the resonance of the CH_3 groups in the TPA unit and the methylene protons of the octyl groups adjacent to C-9 of the fluorene units, respectively.

The SEC traces displayed narrow peaks at 27.04 and 26.85 min corresponding, respectively, to an M_n value of 6190 Da with a M_w/M_n value of 1.02 for PF_3-TPA_3 and an M_n value of 6180 Da with a M_w/M_n value of 1.05 for PF_3-TPA. The M_n values determined from the SEC analysis were based on polystyrene standards. The absolute molecular weights of the products were verified by MALDI-TOF mass spectroscopy. The MALDI-TOF mass spectra displayed a single peak at m/z = 6275.9 for PF_3-TPA_3 and one at m/z = 6215.2 for PF_3-TPA, proving the monodisperse molecular weights of the final products with values consistent with the theoretical values of m/z = 6276.6 for PF_3-TPA_3 and m/z = 6215.5 for PF_3-TPA.

Thermal and Photophysical Properties

The thermal properties of PF_3-TPA_3 and PF_3-TPA were characterized by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) and the results are summarized in Table 1. The DSC curves showed a glass transition at 72 °C for PF_3-TPA_3 and 75 °C PF_3-TPA. No first-order transition related to a crystalline structure was observed in the tested temperature range of –50 to 300 °C, which indicates an amorphous nature of the oligomers. According to the literature, poly(dioctylfluorene) (POF) displays a high crystallization tendency; forming crystals at a low temperature (113 °C).[10] These results indicate that the introduction of the triphenylamine-based core into the oligomers (as a spacer) indeed effectively prevents close-packing of the molecules. On the other hand, a small broad exothermal peak was observed when the temperature was above 200 °C, which might be related to a degradation process of the oligomers. But the TGA analysis did not show any apparent weight loss at these temperatures; indeed, 5% weight loss was observed at about 420 °C.

The UV/Vis absorption and photoluminescence (PL) spectra of solution and film samples of PF_3-TPA_3 and PF_3-TPA were measured and the thermal stabilities of the PL spectra of the films were also studied by annealing the spin-coated PF_3-TPA_3 and PF_3-TPA films on quartz slides in a vacuum at 100 °C for 24 h. The results are shown in Figure 1 and Figure 2. A broad strong absorption band is observed in the solution spectrum with the same absorption maximum at 368 nm for PF_3-TPA_3 and PF_3-TPA. Both materials exhibit very strong fluorescence in the pure-blue region. In addition, there is a negligible shift in the absorption and PL spectra for both steric oligomers on changing from the solution to solid state, which indicates the absence of strong interchain interactions in the solid-state films. Clearly, the novel steric molecular architecture retains an isolated-molecule emission in the condensed state. This is important for enhancing LED performance.[9k] The solid-state PL quantum efficiencies of PF_3-TPA_3 and PF_3-TPA were measured in an integrating sphere according to a literature procedure[14] and were found to be 67 and 86%, respectively. These values are much higher than those of triphenylamine-substituted linear polyfluorenes and poly(dialkylfluorenes), which showed efficiencies of 22–50 and around 50%, respectively.[8a,8d,8f]

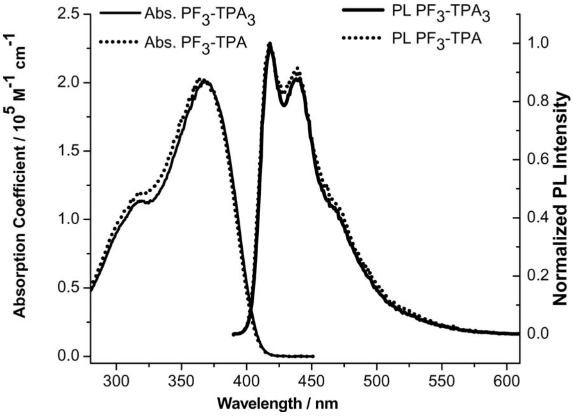


Figure 1. UV/Vis absorption and PL spectra of PF_3-TPA_3 and PF_3-TPA in dichloromethane.

Table 1. Thermal and optical properties of PF_3-TPA_3 and PF_3-TPA.

Oligomer	T_g [°C]	$T_{d\,5\%}$ [°C]	λ_{max} [nm] Solution UV	Solution PL	Film UV	Film PL	ϕ (film) [%]	λ_{max} [nm] Film PL*[a]
PF_3-TPA_3	72	420	368	418, 438	365	420, 441	67	417, 438
PF_3-TPA	75	425	368	417, 439	370	417, 439	86	420, 440

[a] Film PL* after thermal annealing.

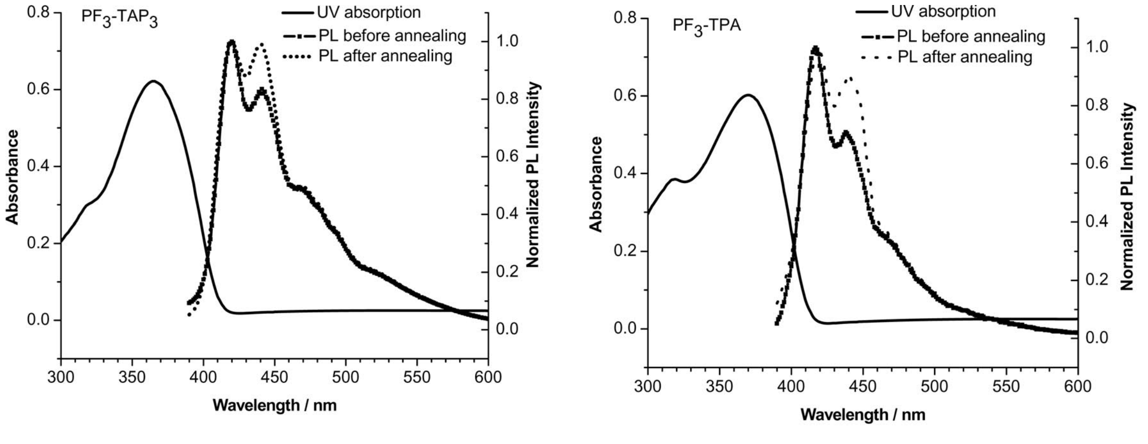


Figure 2. UV/Vis absorption and PL spectra of PF_3-TPA_3 and PF_3-TPA thin films (75 nm) before and after annealing.

After thermal annealing only changes in the relative intensity were observed in the vibronic peaks with the emission peak positions remaining almost unchanged. The PL efficiencies of PF_3-TPA_3 and PF_3-TPA after thermal annealing changed slightly to 64 and 85%, respectively. Moreover, no additional PL peak was observed between 500 and 600 nm in the spectra of PF_3-TPA_3 and PF_3-TPA_3 films, as often appear in the PL spectra of poly(dialkylfluorene) films after thermal annealing. These results demonstrate that the incorporation of triphenylamine-based cores into the fluorene units exert a spacer function, improving thermal and morphological stability and preventing chain aggregation effectively. Even after the films were annealed at 130 °C in air for 24 h, the PL spectra for both compounds remained largely the same (see the Supporting Information), however, a tiny shoulder peak at around 520 nm associated with fluorenone defects was evident.

Cyclic Voltammetry

Cyclic voltammetry (CV) was used to investigate the ionization potentials (E_{HOMO}), the electron affinities (E_{LUMO}) and the electrochemical stabilities of PF_3-TPA_3 and PF_3-TPA. The thin films of oligomers PF_3-TPA_3 and PF_3-TPA were measured in a 0.1 M Bu_4NPF_6/acetonitrile solution at a scan rate of 50 mV/s at room temperature. The CV curves were referenced to an Ag quasi-reference electrode, which was calibrated using an internal standard, the ferrocene/ferrocenium redox couple (0.34 V vs. SCE).[5] According to de Leeuw et al.,[15] the ionization potential (E_{LUMO}) and electron affinity (E_{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 by using the equations $E_{\mathrm{HOMO}} = -(E_p' + 4.38)$ eV and $E_{\mathrm{LUMO}} = -(E_n' + 4.38)$ eV, respectively, in which E_p' and E_n' are the onset potentials for oxidation and reduction relative to the Ag quasi-reference electrode.

The thin films of PF_3-TPA_3 and PF_3-TPA have typical CV curves similar to those reported previously for fluorene polymers.[5,16] Figure 3 shows that both the p- and n-doping processes for PF_3-TPA_3 and PF_3-TPA_3 are reversible. Under successive multiple potential scans, as shown in Figure 3, the PF_3-TPA film only showed a very small decrease in the current intensity in the n-doping process with the CV curve remaining almost unchanged after 10 scans, which indicates good stability towards both electrochemical oxidation and reduction. However, the PF_3-TPA_3 film showed lower stability in the n-doping process. Both oligomer films displayed a 15–30% loss of current intensity after 10 successive p-doping scans. The decrease in the current on cycling arises from the fact that PF_3-TPA and PF_3-TPA_3 are not polymers but short oligomers that are somewhat soluble in their neutral or charged forms in the solvent used. Thus, on cycling, partial dissolution of the material in the films might occur. The onset oxidation (E_p') and reduction (E_n') potentials of PF_3-TPA_3 and PF_3-TPA are 0.98 and –2.10 eV, and 0.90 and –2.08 eV respectively. These values correspond to an E_{HOMO} of –5.36 eV and an E_{LUMO} of –2.28 eV for PF_3-TPA_3 and an E_{HOMO} of –5.28 eV and an E_{LUMO} of –2.20 eV for PF_3-TPA, which are similar to those of triphenylamine-substituted linear polyfluorenes.[8a] These data indicate that the energy barriers for hole-injection from the ITO anode (W_{ITO} = –4.8 eV) to these oligofluorenes are significantly lower than that to the fluorene homopolymer.[16] Traditionally, the introduction of triphenylamine units into conjugated polymers or organic molecules was found to effectively enhance the hole-injecting properties of the resulting materials. At the same time, it also causes an increase in the LUMO energy level, which results in an increased energy barrier for electron injection from the metal cathode. The existence of the triphenylamine units in PF_3-TPA_3 and PF_3-TPA does not apparently lead to this effect. It effectively increased the HOMO level, but maintained the LUMO energy level at about –2.20 eV, comparable to that of the fluorene homopolymer.[16a] This result indicates that introducing a non-conjugated triphenylamine

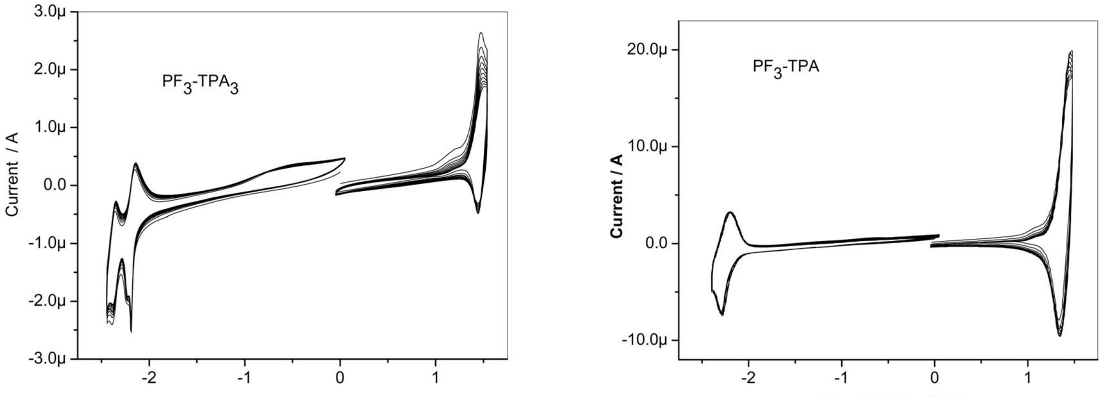


Figure 3. CV curves of the thin films of oligomers PF_3-TPA_3 and PF_3-TPA measured in a 0.1 M Bu_4NPF_6/acetonitrile solution at a scan rate of 50 mV/s at room temperature (10 successive scans vs. an Ag quasi-reference electrode).

unit core into the oligomers promotes their hole-injection capability, but does not sacrifice their electron-injection capability.

Electroluminescence Spectra

Two multi-layer devices with a configuration of ITO/PEDOT-PSS/PF_3-TPA_3 and PF_3-TPA/TPBI/LiF/Al were fabricated to investigate the electroluminescence (EL) properties of the two synthesized compounds. In these devices, poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT-PSS) is a hole-injection layer and wide-band-gap 1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene (TPBI) functions as a hole-blocking and electron-transporting layer. The EL spectra of PF_3-TPA_3 and PF_3-TPA are shown in Figure 4. At low voltages, these oligofluorenes exhibit deep-blue EL, however, the low-energy peak at around 580 nm increased in intensity with applied biases. For PF_3-TPA_3, the CIE chromaticity coordinate is (0.192, 0.101) at 5 V, but changes to (0.226, 0.137) at 6 V and (0.257, 0.168) at 7.5 V. PF_3-TPA was more stable than PF_3-TPA_3: at 5 V, the CIE coordinate of PF_3-TPA is (0.178, 0.069) and at 8 V the CIE coordinate became (0.269, 0.156). At the moment, the reason for this instability is not very clear because this low-energy emission peak was not observed even in the PL spectra of the annealed films. Jen and co-workers also observed a similar EL emission peak at 580 nm for polyfluorenes with triphenylamine and oxadiazole pendant groups at the 9-position of the fluorene units.[8f] At first, we assigned this emission band to fluorenone defects arising from electro-oxidation of the fluorene units. However, numerous literature data indicate that the emission from fluorenone defects should appear at 520–540 nm.[17] Therefore, the appearance of this low-energy emission band may be due to the formation of exciplexes between the emitting layer and TPBI during device operation.

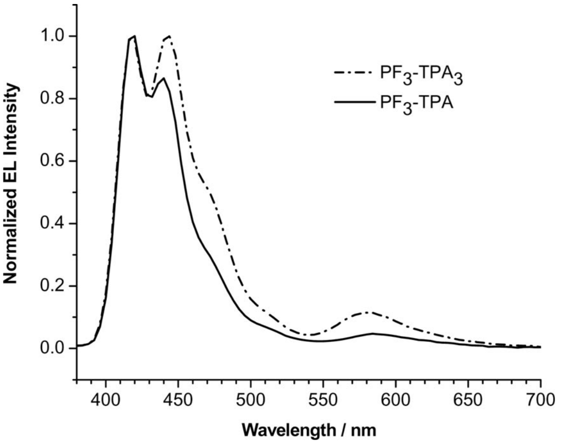


Figure 4. The EL spectra of oligomers PF_3-TPA_3 and PF_3-TPA at 5 V.

The luminance–voltage (*L–V*) and luminous efficiency–voltage (*LE–V*) characteristics of the fabricated devices are outlined in Figure 5. Both compounds show a low turn-on voltage of 4 V. The luminances reached 160 cd/m^2 in the PF_3-TPA_3 device and 56 cd/m^2 in the PF_3-TPA device at 5 V. The EL efficiencies at this luminance are 1.44 and 1.36 cd/A, respectively. Compared with POF,[10] these results suggest that introducing a non-conjugated triphenylamine unit into a fluorene side-chain helps to improve the efficiency of hole injection and transport. Both compounds had a higher luminous efficiency of around 1.5 cd/A (at 6–8 V), which may be attributed to their higher solid-film PL efficiencies. In addition, more current can be injected into the PF_3-TPA_3-based device at the same applied voltages compared with the PF_3-TPA-based device, which leads to a higher luminance. For example, at 7.5 V the luminance of the PF_3-TPA_3-based device already reached 1946 cd/m^2, whereas the PF_3-TPA-based device gave 1055 cd/m^2 at 8 V. These values are comparable to the literature data for triphenylamine-substituted linear polyfluorene derivatives for solution-processed light-emitting devices.[8a,8b,8d,8f]

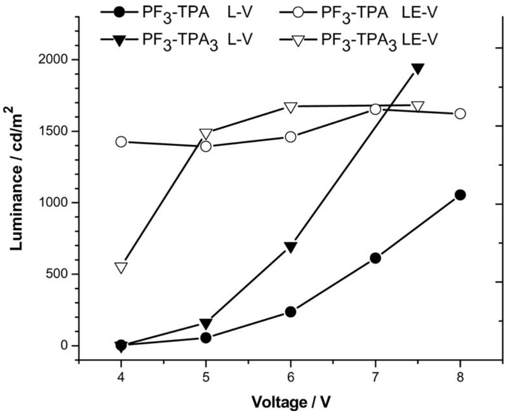


Figure 5. *L–V* and *LE–V* characteristics of the devices prepared from oligomers PF_3-TPA_3 and PF_3-TPA.

Conclusions

Two 3D steric monodisperse oligofluorenes with a TPA_3 and TPA core (PF_3-TPA_3 and PF_3-TPA) have been synthesized by the Friedel-Crafts copolycondensation reaction. The triphenylamine-based cores serve as non-conjugated spacers bearing oligofluorene arms in a multi-H-shaped structure of oligomers such that the optoelectronic properties of the individual oligofluorene arms remain relatively unperturbed. Both oligomers show excellent thermal stability and high photoluminescence quantum efficiency. Electrochemical analysis showed that the non-conjugated triphenylamine core promotes the hole-injection capability of the oligomers, but does not sacrifice their electron-injection capability. LED devices based on these two oligomers showed comparable performances with respect to triphenylamine-substituted linear polyfluorene derivatives in solution-processed light-emitting devices.

Experimental Section

General: The ^{1}H NMR spectra of the materials were recorded with a Bruker spectrometer (500 MHz) in $CDCl_3$ and tetramethylsilane was used as the internal standard. Differential scanning calorimetric (DSC) measurements were performed with a DSC 2920 TA Instrument. Thermogravimetric analyses (TGA) were performed using a Perkin–Elmer Thermal Analysis system. The heating rate was 10 °C/min for DSC measurements and 20 °C/min for TGA measurements in nitrogen. Positive-ion MALDI-TOF/TOF mass spectrometry was performed using an Autoflex II TOF/TOF time-of-flight mass spectrometer (Bruker Daltonics, Germany). The sample solutions were prepared by dissolving sample (0.5 mg) in dichloromethane (0.5 mL), which was then mixed with the matrix solution (50% acetonitrile with 0.5% trifluoroacetic acid solution saturated with cinnamonic acid, 0.05 mL). Size-exclusion chromatography (SEC) was performed at room temperature with a Waters 515 instrument equipped with a Waters 2487 Ultraviolet absorbance detector and a Wyatt Technology Optilab rEX refractive index detector. Styragel HR3, HR4 and HR5 (300 × 7.8 mm) columns from Waters were used. HPLC-grade THF was used as eluent at a flow rate of 1 mL/min. The sample solutions were filtered through a 0.45 µm filter (Nylon, Millex-HN 13 mm Syringes Filters, Millipore, U.S.). The columns were calibrated by using polystyrene standards with molecular weights in the range of 900 and 1.74×10^6 g/mol. UV/Vis absorption spectra were collected with a Shimadzu MPC-3100 UV/Vis/NIR spectrophotometer. Fluorescence measurements were performed with 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 oligomers spin-coated on quartz slides were measured with a Spex Fluorolog 3 spectrometer combined with an integrating sphere according to the literature procedure.[14]

Cyclic voltammetry (CV) measurements were conducted at room temperature in a 0.1 M Bu_4NPF_6/acetonitrile solution using a gas-tight electrochemical cell under the protection of argon with a Solartron SI 1287 potentiostat at a scan rate of 50 mV/s. A silver wire (ϕ = 1 mm), a platinum wire (ϕ = 0.5 mm) and a platinum disk (ϕ = 1 mm) sealed in a soft glass rod were used as the quasi-reference electrode, counter-electrode and working electrode, respectively. The working electrode was coated with the polymer film using a toluene solution and heated in an oven at 80 °C for 5 min. After the cell had been evacuated and filled with argon three times, a 0.1 M Bu_4NPF_6 solution in anhydrous acetonitrile was loaded.

EL Device Fabrication and Testing: ITO-coated glass substrates (15 Ω/square) were patterned by a conventional wet-etching process using a 1:1 mixture of HCl (6 N)/HNO_3 (0.6 N) as the etchant. The active area of each device was 5.5×6.5 mm^2. After patterning, the substrates were rinsed in deionized water and then sequentially subjected to ultrasound in acetone (20 °C) and 2-propanol (65 °C). Immediately prior to device fabrication, the ITO substrate was treated with UV/ozone for 15 min. PEDOT-PSS (50 nm) was spin-coated at 5000 rpm from its aqueous suspension onto the treated substrate and then baked at 135 °C under nitrogen for 30 min. Subsequently, a 1% PF_3-TPA_3 or PF_3-TPA solution in $CHCl_3$ was spin-coated on top of PEDOT-PSS. The resulting film was about 60 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 by using a combination of a Photo Research PR-650 SpectraScan and a Keithley 238 Source meter.

Materials: Tetrahydrofuran, diethyl ether and toluene were dried by Na and distilled prior to use. (4-Bromophenyl)di-*p*-tolylamine was supplied by Zhenjiang Haitong Chemical industry Co., Ltd, China. All other reagents were purchased from Alfa Aesar and used without further purification. (4-Bromophenyl)(phenyl)*p*-tolylamine,[18] 2,7-dibromofluorenone[19] and 9,9,9′,9′-tetra-*n*-octyl-2,2′-bifluorenyl-7-boronic acid[20] were prepared according to literature procedures.

4-[Phenyl(*p*-tolyl)amino)]phenylboronic Acid (1): *n*BuLi (2.5 M in *n*-hexane, 6 mL, 15 mmol) was slowly added to a solution of (4-bromophenyl)(phenyl)*p*-tolylamine (3.88 g, 11.5 mmol) in anhydrous tetrahydrofuran (30 mL) at –78 °C under nitrogen. The reaction mixture was stirred for 1 h before the addition of triisopropoxyborane (8 mL, 6.5 g, 34.5 mmol). The solution was then allowed to warm to room temperature, stirred overnight and then quenched with 2.0 M HCl (25 mL). The aqueous layer was extracted with diethyl ether three times. The combined organic layers were washed with brine before drying with anhydrous Na_2SO_4. The crude product was collected by evaporating the solvent and then purified by column chromatography on silica gel to afford 4-[phenyl(*p*-tolyl)-amino]phenylboronic acid as a white solid (1.85 g, 53%). ^{1}H NMR (500 MHz, [D$_6$]acetone): δ = 2.32 (s, 3 H, CH_3), 6.94 (d, J = 8.5 Hz, 2 H, ArH), 7.00 (d, J = 8.3 Hz, 2 H, ArH), 7.05–7.08 (m, 3 H, ArH), 7.16 (d, J = 8.2 Hz, 2 H, ArH), 7.27–7.33 (m, 2 H, ArH), 7.76 (d, J = 8.5 Hz, 2 H, ArH) ppm. $C_{19}H_{18}BNO_2$ (303.16): calcd. C 75.27, H 5.98, N 4.62; found C 75.36, H 5.89, N 4.72.

1,3,5-Tris{4-[phenyl(*p*-tolyl)amino]phenyl}benzene (TPA_3, 2): 1,3,5-Tribromobenzene (0.37 g, 1.18 mmol), compound **1** (1.38 g, 4.55 mmol) and Aliquat 336 (20% by weight of the monomer) were added to a mixture of toluene (10 mL) and a 2.0 M aqueous solution of Na_2CO_3 (10 mL) in a 100 mL flask. The mixture was evacuated and filled with nitrogen three times. [Pd(PPh$_3$)$_4$] (0.005 equiv.) was then added under nitrogen. The reaction mixture was stirred under reflux for 24 h. The organic layer was then separated, dried with anhydrous Na_2SO_4 and concentrated by evaporating the solvent prior to further purification by column chromatography on silica gel to afford TPA_3 as a pale-yellow solid (0.83 g, 83%). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 2.29 (s, 9 H, CH_3), 6.90–7.10 (m, 21 H, ArH), 7.17, (d, J = 7.7 Hz, 6 H, ArH), 7.31 (m, 6 H, ArH), 7.72–7.82 (m, 9 H, ArH) ppm. MS (AutoflexTOF/TOF): m/z = 849.3. $C_{63}H_{51}N_3$ (850.10): calcd. C 89.01, H 6.05, N 4.94; found C 88.98, H 6.12, N 4.86.

2,7-Dibromo-9-(*p*-tolyl)fluoren-9-ol (3): *n*BuLi (2.5 M in *n*-hexane, 9.1 mL, 22.79 mmol) was slowly added to a solution of 1-bromo-4-methylbenzene (3.39 g, 19.82 mmol) in anhydrous tetrahydrofuran (15 mL) at –78 °C under nitrogen. The reaction mixture was then stirred for 1 h before the addition of 2,7-dibromofluorenone (6.03 g, 17.84 mmol) in anhydrous tetrahydrofuran (50 mL). The solution was then allowed to warm to room temperature, stirred overnight and quenched with 2.0 M HCl (30 mL). The aqueous layer was extracted with diethyl ether three times. The combined organic layers were dried with anhydrous Na_2SO_4. The crude product was collected by evaporating the solvent and then purified by column chromatography on silica gel to afford **3** as a light-yellow solid (5.60 g, 73%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.35 (s, 3 H, CH_3), 7.14 (d, J = 7.4 Hz, 2 H, ArH), 7.25 (d, J = 8.0 Hz, 2 H, ArH), 7.38–7.55 (m, 6 H, ArH) ppm. MS (AutoflexTOF/TOF): m/z = 430.2. $C_{20}H_{14}Br_2O$ (430.13): calcd. C 55.85, H 3.28; found C 55.94, H 3.21.

Pentafluorene (4): Compound **3** (0.33 g, 0.76 mmol), 9,9,9′,9′-tetra-*n*-octyl-2,2′-bifluorenyl-7-boronic acid (1.50 g, 1.82 mmol) and Aliquat 336 (20% by weight of the monomer) were added to a mixture of toluene (15 mL) and a 2.0 M aqueous solution of Na_2CO_3 (10 mL) in a 100 mL flask. The mixture was evacuated under vacuum and filled with nitrogen three times. [$(PPh_3)_4Pd^0$] (0.005 equiv.) was then added under nitrogen. The reaction mixture was stirred under reflux for 24 h. The organic layer was then separated, dried with anhydrous Na_2SO_4 and concentrated by evaporating the solvent prior to further purification by column chromatography on silica gel to afford **4** as a pale-yellow solid (0.85g, 62%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.68–0.87 (m, 40 H, CH_2CH_3), 1.07–1.27 (m, 80 H, $CH_2CH_2CH_2CH_2CH_2$), 2.03–2.13 (m, 16 H, CH_2), 2.36 (s, 3 H, CH_3), 7.17–7.19 (d, *J* = 8.0 Hz, 2 H, ArH), 7.34–7.42 (m, 6 H, ArH), 7.48 (d, *J* = 8.0 Hz, 2 H, ArH), 7.58–7.86 (m, 26 H, ArH) ppm. MS (AutoflexTOF/TOF): *m*/*z* = 1826.8. $C_{136}H_{176}O$ (1826.85): calcd. C 89.41, H 9.71; found C 89.28, H 9.65.

Oligomer PF_3-TPA_3: Compound **4** (0.505 g, 0.2765 mmol) and **2** (67.80 mg, 0.0798 mmol) were dissolved in mesitylene (7 mL) in a 50 mL flask and 1 drop of *p*-toluenesulfonic acid was added. The reaction mixture was stirred at 80 °C for 3 h under nitrogen and was then concentrated by evaporating the solvent prior to further purification by column chromatography on silica gel to afford PF_3-TPA_3 as a pale-yellow solid (0.365 g, 73%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.73–0.92 (m, 120 H, CH_2CH_3), 1.08–1.28 (m, 240 H, $CH_2CH_2CH_2CH_2CH_2$), 2.06–2.15 (m, 48 H, CH_2), 2.30 (s, 9 H, CH_3), 2.33 (s, 9 H, CH_3), 7.02 (d, *J* = 7.7 Hz, 6 H, ArH), 7.05–7.20 (m, 24 H, ArH), 7.24 (d, *J* = 7.9 Hz, 6 H, ArH), 7.32–7.39 (m, 24 H, ArH), 7.50 (d, *J* = 6.5 Hz, 6 H, ArH), 7.57–7.82 (m, 75 H, ArH), 7.90 (d, *J* = 7.7 Hz, 6 H, ArH) ppm. MS (AutoflexTOF/TOF): *m*/*z* = 6275.9. $C_{471}H_{573}N_3$ (6276.61): calcd. C 90.13, H 9.20, N 0.67; found C 90.07, H 9.15, N 0.63.

2,7-Dibromo-9-[4-(4,4′-dimethyldiphenylamino)phenyl]fluoren-9-ol (5): *n*BuLi (2.5 M in *n*-hexane, 3.7 mL, 9.17 mmol) was slowly added to a solution of (4-bromophenyl)di-*p*-tolylamine (2.81 g, 7.98 mmol) in anhydrous tetrahydrofuran (20 mL) at –78 °C under nitrogen. The reaction mixture was stirred for 1 h before the addition of 2,7-dibromofluorenone (2.70 g, 7.98 mmol) in anhydrous tetrahydrofuran (45 mL). The solution was then allowed to warm to room temperature, stirred overnight and then quenched with 2.0 M HCl (20 mL). The aqueous layer was extracted with diethyl ether three times. The combined organic layers were dried with anhydrous Na_2SO_4. The crude product was collected by evaporating the solvent, which was then purified by column chromatography on silica gel to give **5** as a yellow solid (2.50 g, 51%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.38 (s, 6 H, CH_3), 6.92 (d, *J* = 8.0 Hz, 2 H, ArH), 7.01 (d, *J* = 8.0 Hz, 4 H, ArH), 7.08 (d, *J* = 8.0 Hz, 4 H, ArH), 7.16 (d, *J* = 8.0 Hz, 2 H, ArH), 7.49–7.55 (m, 6 H, ArH) ppm. MS (AutoflexTOF/TOF): *m*/*z* = 611.1. $C_{33}H_{25}NOBr_2$ (611.37): calcd. C 64.83, H 4.12, N 2.29; found C 64.68, H 4.19, N 2.20.

Pentafluorene (6): Compound **5** (0.95 g, 1.55 mmol), 9,9,9′,9′-tetra-*n*-octyl-2,2′-bifluorenyl-7-boronic acid (3.52 g, 4.28 mmol) and Aliquat 336 (20% by weight of the monomer) were added to a mixture of toluene (30 mL) and a 2.0 M aqueous solution of Na_2CO_3 (20 mL) in a 100 mL flask. The mixture was evacuated and filled with nitrogen three times. [$(PPh_3)_4Pd^0$] (0.005 equiv.) was then added under nitrogen. The reaction mixture was stirred under reflux for 24 h. The organic layer was then separated, dried with anhydrous Na_2SO_4 and concentrated by evaporating the solvent prior to further purification by column chromatography on silica gel to afford **6** as a pale-yellow solid (1.74 g, 56%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.72–0.92 (m, 40 H, CH_2CH_3), 1.14–1.22 (m, 80 H, $CH_2CH_2CH_2CH_2CH_2$), 2.04–2.16 (m, 16 H, CH_2), 2.30 (s, 6 H, CH_3), 6.95–7.10 (m, 10 H, ArH), 7.32–7.45 (m, 8 H, ArH), 7.62–7.88 (m, 26 H, ArH) ppm. MS (AutoflexTOF/TOF): *m*/*z* = 2008.5. $C_{149}H_{187}NO$ (2008.09): calcd. C 89.12, H 9.39, N 0.70; found C 89.01, H 9.45, N 0.63.

Oligomer PF_3-TPA: Compound **6** (0.87 g, 0.43 mmol) and triphenylamine (31.8 mg, 0.13 mmol) were dissolved in mesitylene (10 mL) in a 100 mL flask and 1 drop of *p*-toluenesulfonic acid was added. The reaction mixture was stirred at 80 °C for 3 h under nitrogen and was then concentrated by evaporating the solvent prior to further purification by column chromatography on silica gel to afford oligomer PF_3-TPA as a pale-yellow solid (0.71 g, 88%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.75–0.85 (m, 120 H, CH_2CH_3), 0.95–1.23 (m, 240 H, $CH_2CH_2CH_2CH_2CH_2$), 1.95–2.05 (m, 48 H, CH_2), 2.22 (s, 18 H, CH_3), 6.82–6.97 (m, 30 H, ArH), 7.05 (d, *J* = 8.5 Hz, 6 H, ArH), 7.13 (d, *J* = 7.0 Hz, 6 H, ArH), 7.32–7.39 (m, 24 H, ArH), 7.46–7.56 (m, 18 H, ArH), 7.62–7.78 (m, 54 H, ArH), 7.85 (d, *J* = 8.0 Hz, 6 H, ArH) ppm. MS (AutoflexTOF/TOF): *m*/*z* = 6215.2. $C_{465}H_{570}N_4$ (6215.53): calcd. C 89.86, H 9.24, N 0.90; found C 89.73, H 9.30, N 0.83.

Supporting Information (see also the footnote on the first page of this article): ^{1}H NMR spectra, SEC traces, MALDI-TOF mass spectra, DSC curves, TGA curves and PL spectra of oligomers after annealing.

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