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Hyperbranched Blue-Light-Emitting Alternating Copolymers of Tetrabromoarylmethane/Silane and 9,9-Dihexylfluorene-2,7-diboronic Acid

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ABSTRACT: The first soluble hyperbranched tetrahedral polymers were prepared by Suzuki coupling polycondensation reaction between tetrabromoarylmethane/silane and 9,9-dihexylfluorene-2,7-diboronic acid at low concentrations. The polymers exhibited high thermal stability with their decomposition temperatures (T_ds) in the range 352−449 °C. The polymers emitted blue light highly efficiently in both solution and the solid state. The photoluminescence quantum efficiencies of the polymers in THF solution were in the range 73−99%, and those in thin films were 38−82%. The film PL spectra of the polymers exhibited similar spectral patterns to those determined in solutions, with 1−8 nm red shift in their emission maxima and 0−8 nm increase in their full width at half-maximum (fwhm) values being observed. No long wavelength excimer-like emissions at 500−600 nm, which were typical for polyfluorenes due to their self-aggregation in the solid state, were observed. Thus, the polymers were less prone to self-aggregation in the solid state due to their hyperbranched structures. A double-layer polymer light-emitting diode (PLED) device with a configuration of ITO/PEDOT/polymer/LiF/Ca/Ag was fabricated. The device showed bright blue emission peaking at 415 nm with an external quantum efficiency of 0.6% and a turn voltage at 6.0 V. The synthetic simplicity, good solubility and solution processability, high PL quantum efficiencies in solution and the solid state, and nonaggregating property in the solid state would make the present polymers a novel class of blue emitters.

Introduction

During the past decade, many studies on organic light-emitting materials have been focused on developing efficient, stable, and pure blue-light-emitting polymers.[1] Polyfluorene derivatives (PFs) have proven by far the most promising ones.[2] However, the performances of PFs as blue emitters have been hampered by their tendencies of forming aggregates, excimers, or ketone defects during either annealing or passage of current, which lead to red-shifted and less efficient emission and reduced color purity.[3] Recently, studies on light-emitting tetrahedral molecular glass materials[4] and polymeric materials,[5] cross-linked oligofluorene networks,[6] and Si-containing hyperbranched polymers[7] have been investigated to address the above problems. Such luminescent materials are not only less prone to self-aggregation in the solid state due to their hindered structures but also emit purer blue light as the interruption of the regular π-conjugated system by the δ-C/Si atoms in the tetrahedral cores prevents the red shift of blue emission associated with the increase in conjugation length.[8] We have previously reported a series of luminescent tetraphenylmethane−oligothiophene conjugates and their water-soluble poly(ethylene glycol)-linked polymers.[9] In this paper, we report the synthesis, thermal, optical, and electroluminescent properties of several hyperbranched tetrahedral polymers prepared from Suzuki coupling polycondensation reaction between X(*p*-ArBr)$_4$ (X = C, Si; Ar = $-C_6H_4-$, $-C_6H_4C_6H_4-$) and 9,9-dihexylfluorene-2,7-diboronic acid at low concentrations. These polymers were soluble in common organic solvents (THF, DMF, and chloroform) and showed excellent thermal stabilities. They emitted bright violet-blue light with high PL quantum efficiencies in both solution and the solid state. The emission spectra of the polymers in the solid state exhibited similar spectral patterns to those determined in solution, which were revealed by a small red shift (1−8 nm) in their emission maxima and similar full width at half-maximum (fwhm) values. A double-layer polymer light-emitting diode (PLED) device was fabricated, and preliminary results on the device performance are reported.

Results and Discussion

Synthesis and Characterization. Recently, several tetrahedral core compounds such as tetraphenylmethane and tetraphenylsilane have been intensively employed as building blocks for the synthesis of optoelectronic materials.[4,10] For such syntheses, the tetrabromo derivatives of tetraphenylmethane/silane have been the most widely used precursors. Whereas direct bromination of tetraphenylmethane with neat bromine efficiently yielded tetra(4-bromophenyl)methane (**1**),[11] preparation of similar bromo derivatives of tetraarylsilane proved to be more difficult.[12] Scheme 1 shows the synthesis of the two tetrabromoarylsilanes **2** and **3**. First, we tried to synthesize these two precursors by monolithiation of Br−Ar−Br with *n*-BuLi and subsequent substitution reaction with $SiCl_4$ or $Si(OEt)_4$ at −20 °C. The above reactions yielded (*n*-Bu)−Ar−Br as major products in nearly 70% yields and disubstituted products (*n*-Bu)−Ar−(Bu-*n*) in <10% yields. The products were purified by distillation or column chromatography. Their physical data were identical to those

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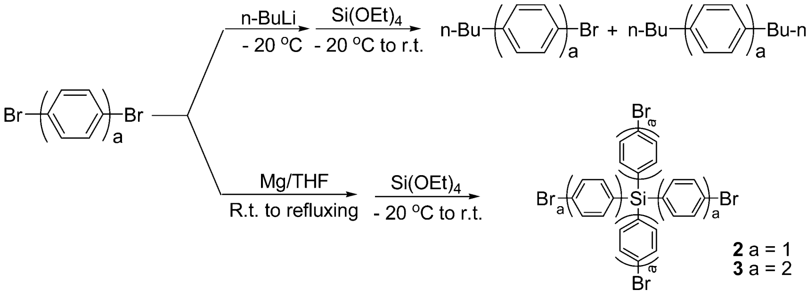
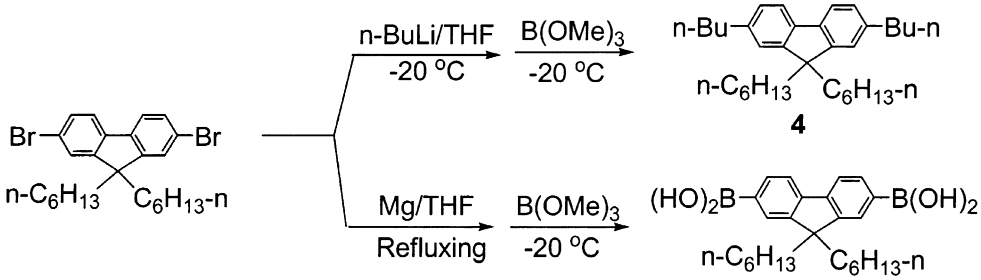
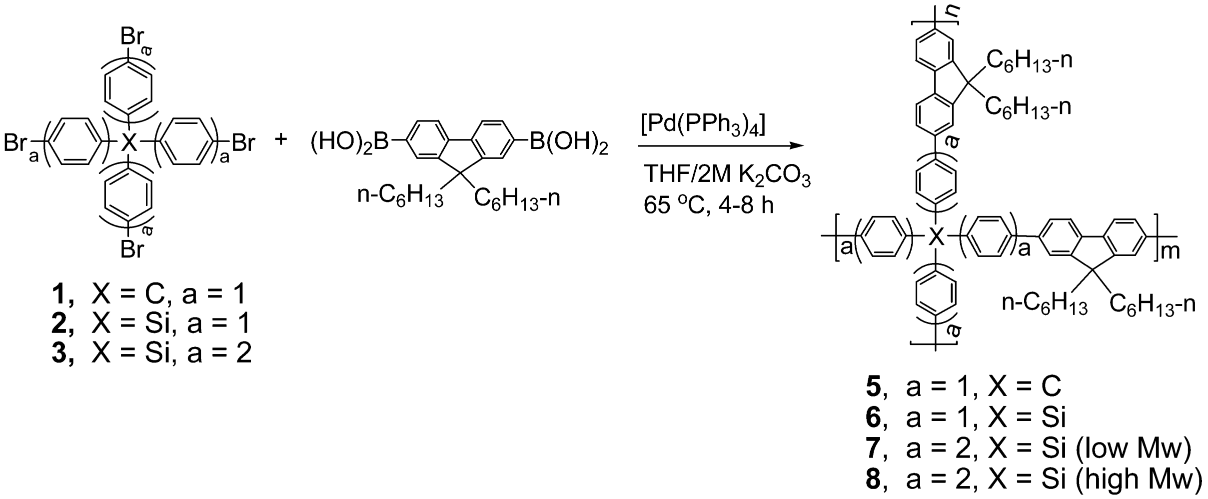
Scheme 1. Synthesis of Tetrabromoarylmethane/Silane



Scheme 2. Synthesis of 9,9-Dihexylfluorene-2,7-diboronic Acid



Scheme 3. Synthesis of the Tetrahedral Polymers 5−8



reported in previous publications.[13] Apparently, the formation of the butyl-substituted products involved the nucleophilic substitution between monolithiate of dibrombenzene/dibromobiphenyl and *n*-BuBr.[14] Alternatively, the precursor compounds **2** and **3** were effectively prepared by the substitution reaction between Br−Ar−MgBr and Si(OEt)$_4$ in good yields. Similarly, the synthesis of 9,9-dihexylfluorene-2,7-diboronic acid was achieved by the substitution of the Grignard reagent of 2,7-dibromo-9,9-dihexylfluorene with B(OMe)$_3$ following a literature method.[15] Preparation of this diboronic acid via dilithiation of 2,7-dibromo-9,9-dihexylfluorene with *n*-BuLi at −20 °C yielded the butyl-disubstituted byproduct **4** in 66% yield (Scheme 2).

The synthetic route to the tetrahedral polymers is shown in Scheme 3. These polymers were prepared by the copolymerization between AB$_4$-type tetrabromo monomers and AB$_2$-type diboronic acid. It has been well established that the use of a multifunctional monomer (AB$_2$ or AB$_3$) in a step-growth polymerization tends to produce insoluble cross-linked polymers. Such a tendency could be avoided or reduced when the polymerization is carried out below the gel point, that is, at a low concentration to prevent full conversion. We first carried out Suzuki coupling polycondensation reactions of the tetrabromo monomer and 9,9-dihexylfluorene-2,7-bis(trimethylene boronate) in a solution of toluene/K$_2$CO$_3$(aq) at 110 °C (monomer concentrations at about 0.5−1.0 M),[16] which yielded insoluble polymers quantitatively. The poor solubility of the polymers might be due to their high molecular weights and hyperbranched rigid structures. Although modeling studies showed that Suzuki cross-coupling of branches is not easy to occur due to the linear steric requirement for the coupling moieties, we carried out Suzuki coupling polycondensation reaction of the tetrabromo monomer with 9,9-dihexylfluorene-2,7-diboronic acid in a dilute solution of THF/K$_2$CO$_3$ at 65 °C (monomer concentrations at ca. 0.005 M, Scheme 3) to reduce the polymerization degrees and possible cross-linking between branches. Such a reaction condition indeed produced soluble polymers. Among the three tetrabromo precursors, compound **3** appeared to be the least reactive one as the polymer **7** was obtained in the lowest molecular weight under the same reaction conditions. Reacting this tetrabromo monomer (**3**) with the diboronic acid for

Table 1. Summary of the Synthesis, Thermal, and Optical Properties of Polymers 5–8

						soln λ_{max} (nm)[b]		film λ_{max} (nm)[c]		Φ_{PL} (%)[f]	
polymer	yield (%)	M_w	M_w/M_n	T_g (°C)	T_d[a] (°C)	abs	em	abs	em	soln	film
5	50	33500	2.43	236	449	334	398, 420[d] (54)[e]	345	399, 420[d] (62)[e]	73	38
6	52	7640	1.15	237	439	332	397 (44)[e]	333	402, 419[d] (52)[e]	92	65
7	35	3920	1.45	235	352	345	404 (48)[e]	353	412, 435[d] (46)[e]	99	78
8	56	7560	1.67	238	380	355	407, 428[d] (45)[e]	374	414, 439[d] (45)[e]	99	82

[a] T_d is defined as the temperature at which a 5% weight loss is recorded by the TGA analysis. [b] In THF solution (ca. 0.1 mg in 100 mL). [c] Spin-coated on quartz plates from THF solutions. [d] Appear as shoulder peaks. [e] Fwhm, nm. [f] The photoluminescent quantum yields (Φ_{PL}) of the polymers in THF were determined using a solution of quinine sulfate (ca. 1 × 10^{-5} M in 0.1 M H_2SO_4, having a quantum yield of 55%) as a standard. The Φ_{PL} values of films were determined using 9,10-diphenylanthracene (dispersed in PMMA films with a concentration lower than 1 × 10^{-3} M and a quantum efficiency of 83%) as a standard.

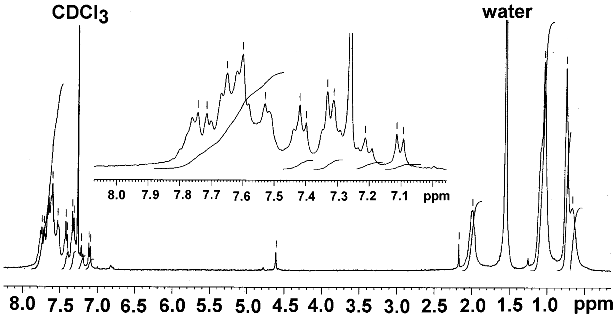


Figure 1. ^1H NMR spectrum of polymer **5** in $CDCl_3$.

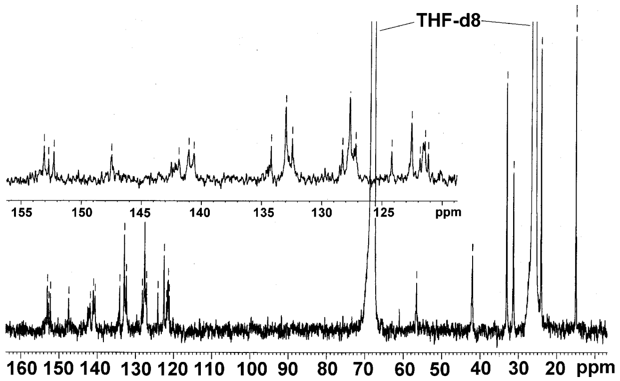


Figure 2. ^{13}C NMR spectrum of polymer **5** in THF-d_8.

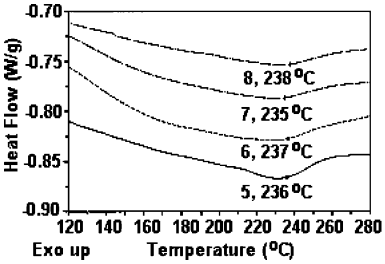


Figure 3. DSC thermograms of polymers **5**–**8** measured under nitrogen at a heating rate of 10 °C/min (recorded during the second heating scan).

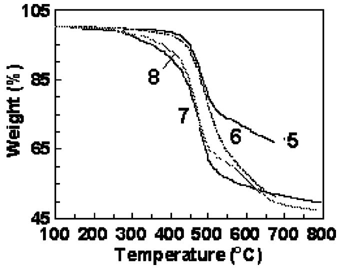


Figure 4. TGA thermograms of polymers **5**–**8**. The thermal analyses were carried out under nitrogen at a heating rate of 20 °C/min.

a longer time with other conditions unchanged gave polymer **8** with a higher molecular weight than **7**. Polymers **5**–**8** were obtained as light yellow powders in 35–56% yields. A summary of the characterization data of polymers **5**–**8** is shown in Table 1. The polymers were soluble in THF, DMF, and chloroform. For example, the solubility of polymer **8** in THF was 15 mg/mL, which permits good solution processability for PLED fabrications. Polymers **5** and **6** were insoluble in acetone and ethanol, whereas **7** and **8** were insoluble in ethanol but slightly soluble in acetone. Continuous Soxhlet extraction of **5** and **6** with acetone and **7** and **8** with ethanol effectively removed catalyst residues and more soluble oligomers. The polymers tended to form inclusion complexes with organic solvents (ethanol and acetone) like other reported tetrahedral materials, possibly due to their porous structures.[17] The solvents could be removed by heating at a higher temperature (>100 °C) under vacuum. All the purified polymers could be completely dissolved in THF, revealing that no cross-linked networks were formed during the polymerization reactions. The chemical structures of polymers **5**–**8** were satisfactorily characterized by ^1H and ^{13}C NMR spectroscopy and microanalysis. Elemental and NMR spectroscopic analyses of the polymers are consistent with chemical compositions similar to the monomer feeds. The typical ^1H NMR and ^{13}C NMR spectra of the polymers are shown in Figures 1 and 2, respectively.

All the polymers exhibited glass transition temperatures (T_g) at 235–238 °C and showed characteristic DSC thermograms of hyperbranched polymers with rigid structures (Figure 3).[18] TGA studies showed that the polymers were thermally stable with their T_ds in the range 352–449 °C, and no weight losses were observed at lower temperatures (Figure 4). All polymers showed similar broad amorphous peaks at ca. $2\theta = 20°$ as revealed by wide-angle X-ray diffraction (WAXD) studies, indicating the amorphous natures of all polymers.

Optical Properties of the Polymers in Solution and the Solid State. Figure 5 shows the UV and PL spectra of polymers **5**–**8** in THF solution and the solid state. A summary of their optical data is given in Table 1. Uniform colorless films were prepared on quartz substrates by spin-coating from solutions in THF (about 1%) at a spin rate of 2000 rpm. The absorbances of the films at their long wavelength maxima were made to be less than 0.1 for accurate PL quantum yield determinations. Upon exposure to UV radiation, the films emitted bright violet-blue light. In THF solution, the polymers exhibited absorption maxima in the range 322–355 nm and emission maxima in the range 397–407 nm with vibrational shoulders at 420–430 nm. Both the absorption and emission maxima of polymers **7** and **8** are significantly red-shifted from those of **5** and **6**,

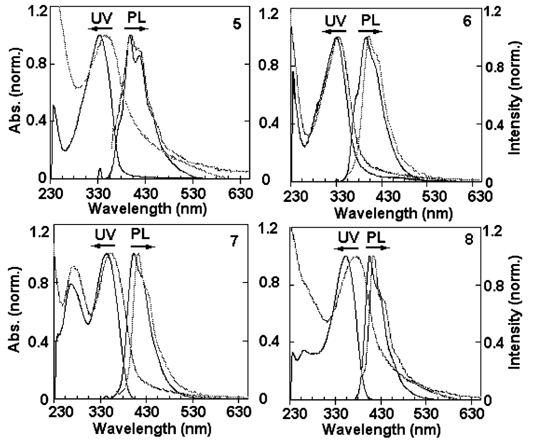


Figure 5. UV and PL spectra of polymers **5**−**8** in THF solutions (solid lines) and in the solid state (dashed lines).

apparently due to the increase in conjugation length. Furthermore, both the absorption and emission maxima of **8** are red-shifted from those of **7**. These red shifts are obviously associated with the higher molecular weight of **8** and might be due to the hyperconjugation through the Si atoms in the tetrahedral cores.[19] This feature is of importance as it would be possible to fine-tune the optical properties of the polymers by their molecular weights, which can be easily controlled by reaction time. The film UV and PL spectra of **5**−**8** show similar spectral patterns to those determined in solution, with 1−19 and 1−8 nm red shifts being observed for their absorption and emission maxima, respectively. The quantum efficiencies of the polymers in the solid state are in the range 38−82%. The film PL spectra of polymers **5** and **6** are slightly broadened, whereas the fwhm values of **7** and **8** in the solid state are essentially the same as those in solution. In addition to the spin-coating method, we also prepared the films of **5**−**7** by a direct dropping method (absorbances at absorption maxima: 0.2−0.5). The UV and PL spectra of the films obtained by this method were essentially the same as those obtained by the spin-coating method. No excimer-like long wavelength emissions in the region of 500−600 nm, which were typical for PFs,[2,3] were observed in the PL spectra of both solution and film samples. It should be noted that all the polymers were dried in a vacuum oven at 120 °C overnight before they were prepared for optical measurements. All these results reveal that the inter- and intramolecular interactions of the polymers are rather weak, resulting in efficient and stable photoluminescences.[4,6] The reduced intermolecular interactions are caused by the nonplanar tetrahedral carbon and silicon atoms. Some light-emitting polyacetylenes also showed similar phenomenon; that is, their luminescence was not quenched in the solid state.[21] It is also of importance to note that the Si-centered polymers exhibited superior photoluminescent efficiencies over that of the C-centered one in both solution and the solid state, possibly due to a stronger tendency of the central Si atoms involving in hyperconjugation.

Electroluminescence Properties. The preliminary studies on the application of the polymers for PLEDs were carried out. Polymer **8** was used as the emitting layer in a double-layer light-emitting device with a configuration of ITO/PEDOT (80 nm)/polymer **8** (50 nm)/LiF (0.5 nm)/Ca (20 nm)/Ag (100 nm). Poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonic acid) (PPS) was used as the hole injection/transporting layer. The active area of the device was about 4.0 mm^2. Figure 6 shows current (*I*) and luminance (*L*) of the device as a function of applied voltage (*V*). The device emitted bright blue light starting at about 6.0 V and reaches a brightness of 78 cd/m^2 at a bias of 8.0 V. The maximum external quantum efficiency was measure to be 0.60% (at 7.5 V with current density of 110 mA/cm^2 and a brightness of 70 cd/m^2). The EL spectrum of the polymer exhibited an emission maximum at 415 nm and a vibrational peak at 437 nm, which are essentially the same as those of its film PL spectrum, indicating that same excitations are involved in both cases (Figure 7).[20] In addition, a very weak peak at 552 nm, which is typical of PFs due to excimer formation,[2,3] is also observed. These preliminary data show the applicability of the present novel polymers as PLED blue-emitters. Detailed studies on device fabrication and performance are currently in progress.

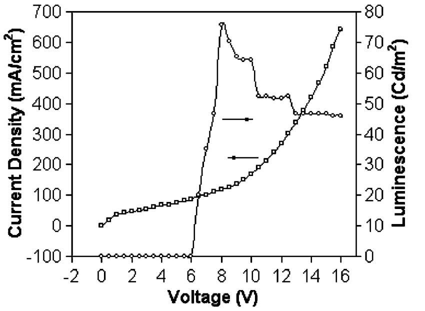


Figure 6. Current−voltage (*I*−*V*) and luminance−voltage (*L*−*V*) curves of an ITO/PEDOT/polymer **8**/LiF/Ca/Ag device.

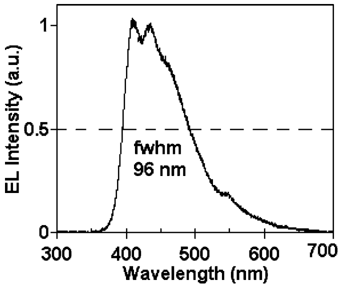


Figure 7. EL spectrum of the device with the configuration ITO/PEDOT/polymer **8**/LiF/Ca/Ag.

Conclusion

Several hyperbranched tetrahedral polymers have been synthesized by facile Suzuki coupling polycondensation reactions between tetrabromoarylmethane/silane and 9,9-dihexylfluorene-2,7-diboronic acid at low concentrations. These polymers were soluble in common organic solvents such as THF and DMF and exhibited excellent thermal stability. The polymers exhibited strong blue fluorescence under excitation by UV light in solution and the solid state. The polymers were less prone to self-aggregation in the solid state due to their hyperbranched structures, and no excimer-like long wavelength emissions were observed in their solution and film PL spectra. A double-layer PLED with a configuration of ITO/PEDOT/polymer/LiF/Ca/Ag was fabricated. The device showed bright blue emission peaking at 415 nm with an external quantum efficiency of 0.6% and a turn voltage at 6.0 V. The synthetic simplicity, good solubility and processability, high PL quantum efficiencies in solution and the solid state, and nonaggregating property in the solid state would make the present polymers a novel class of blue emitters.

Experimental Section

The starting materials 2,7-dibromo-9,9-dihexylfluorene and 9,9-dihexylfluorene-2,7-bis(trimethylene boronate) were prepared according to a literature method.[15,16] Unless stated otherwise, all reagents and solvents were of commercial grade and used as received. All reactions were performed under a purified nitrogen atmosphere. Tetrahydrofuran (THF) was distilled over CaH_2 before use.

The ^1H NMR spectra were recorded at 25 °C on a Bruker AVANCE 400 spectrometer. Mass spectra were recorded on a Finnigan/MAT TSQ 7000 or an ABI Voyager STR spectrometer. UV−vis spectra were measured with a UV−vis spectrometer (Shimadzu, UV-2501 PC) at 20 °C. Fluorescence spectra were recorded on a LS50B luminescence spectrometer (Perkin-Elmer) at 20 °C. Melting points and glass transition temperatures were determined by differential scanning calorimetry (DSC) experiments using a TA 2920 modulated DSC instrument with a ramp speed of 10 °C/min. Thermogravimetric analyses (TGA) were conducted on a Perkin-Elmer thermogravimetric analyzer TGA 7 under a heating rate of 20 °C/min and a nitrogen flow rate of 20 cm^3/min. The photoluminescent quantum yields (Φ_{PL}) of the polymers in THF were determined using a solution of quinine sulfate as a standard (ca. 1×10^{-5} M in 0.1 M H_2SO_4, having a quantum yield of 55%). The Φ_{PL} values of films were determined using 9,10-diphenylanthracene as a standard (dispersed in PMMA films with a concentration lower than 1×10^{-3} M and a quantum efficiency of 83%). WAXS measurements were conducted using Bruker X-ray diffractometer using Cu Kα (λ = 1.541 Å) radiation. The X-ray tube was operated at 40 kV and 40 mA. Elemental analyses were performed by the Elemental Analysis Laboratory of the Department of Chemistry at the National University of Singapore.

A General Procedure for the Synthesis of Si(*p*-ArBr)$_4$. 2,4-Dibromobenzene or 4,4′-dibromobiphenyl (10 g) and magnesium turnings (1.05 equiv of BrArBr) were dissolved in 150 mL of THF. The Grignard reaction was initiated by addition of I_2. The reaction mixture was first stirred at room temperature for 2 h and then was heated at 65 °C overnight to give a brown solution of the Grignard reagent. To a solution of $Si(OEt)_4$ (0.25 equiv of BrArBr) in 50 mL of THF was added the Grignard agent at room temperature. The reaction mixture was stirred at room temperature for 16 h and then refluxed for 4 h. Upon completion, 100 mL of 1 N HCl was added slowly into the reaction mixture. The organic layer was isolated, and the aqueous layer was extracted with dichloromethane (2 × 150 mL). The combined organic solution was washed with brine and dried ($MgSO_4$). Filtration through Celite gives a clear yellow solution. The product was purified by silica gel column chromatography (hexanes/chloroform 2:1).

Tetra(4-bromophenyl)silane (2). A colorless solid 4.3 g (62%). The physical and spectroscopic data were identical to those reported in the literature.[12]

Tetra(4-bromobiphenyl)silane (3). A white solid 3.5 g (51%); mp > 300 °C. Anal. Cacld for $C_{48}H_{32}Br_4Si$: C, 60.3; H, 3.4; Br, 33.4. Found: C, 60.5; H, 3.2; Br, 33.0. ^1H NMR ($CDCl_3$): δ 7.41 (d, 4H, $^3J_{HH} = 8.4$ Hz), 7.46 (d, 4H, $^3J_{HH} = 8.8$ Hz), 7.57 (d, 16H, $^3J_{HH} = 8.4$ Hz). ^{13}C NMR ($CDCl_3$): δ 127.3, 128.0, 128.8, 129.1, 129.2, 132.2, 132.4, 139.2. MALDI−TOF MS, *m*/*e*: 956.67 (M^+, 100%).

Synthesis of 2,7-Dibutyl-9,9-dihexylfluorene (4). 9,9-Dihexyl-2,7-dibromofluorene (5 g, 10 mmol) was dissolved in dry THF (100 mL) and cooled to −20 °C. To the solution was added *n*-BuLi (15 mL, 24 mmol) dropwise. The reaction mixture was stirred at −20 °C for 2 h. To the above solution was then added $B(OMe)_3$ (3.2 mL, 28 mmol) through a springe in one portion. The reaction mixture was stirred at −20 °C for 3 h and warmed to room temperature and continued to stir overnight. After the mixture was cooled to 0 °C, it was quenched with 20 mL of 1 N HCl. The organic layer was isolated, and the aqueous layer was diluted and extracted with diethyl ether. The combined organic solution was washed with water until the aqueous layer became neutral. The organic solution was dried ($MgSO_4$). The product was separated by silica gel column chromatography (hexanes) and was obtained as a light yellow oil (3.1 g, 66.1%). Anal. Cacld for $C_{33}H_{50}$: C, 88.7; H, 11.3. Found: C, 89.0; H, 11.5. ^1H NMR ($CDCl_3$): 0.77 (t, J = 6.8 Hz, 6 H, $2CH_3$), 0.94 (t, J = 7.6 Hz, 6 H, $2CH_3'$), 1.04−1.14 (m, 16 H), 1.36 (q, J = 7.6 Hz, 4 H, $2CH_2$), 1.63 (t, J = 8.0 Hz, 4H, $2CH_2$), 1.89−1.93 (m, 4H, $2CH_2$), 2.68 (t, J = 7.6 Hz, 4H, $2CH_2$), 7.10 (s, 2H, aromatic-H), 7.11 (d, J = 8.0 Hz, 2H), 7.54 (d, J = 8.0 Hz, 2H, aromatic-H). ^{13}C NMR ($CDCl_3$): δ 14.3, 22.6, 22.9, 24.0, 30.0, 31.8, 34.4, 36.3, 40.7, 55.0, 119.3, 123.2, 127.1, 139.2, 141.8, 151.1. MS (EI), *m*/*e*: 446.3 (M^+, 100%).

A General Procedure for the Synthesis of Polymers 5−8. Tetrabromoarylmethane/silane (0.5 g), 9,9-dihexylfluorene-2,7-diboronic acid (2.0 equiv), and $[Pd(PPh_3)_4]$ (1 mol %) were dissolved in THF (112.5 mL) and 2 M K_2CO_3 (aq, 75 mL). The reaction mixture was degassed by bubbling with N_2 and then was heated at 65 °C (oil-bath temperature) for 4 h (**5**−**7**) or 8 h (**8**) under N_2. Upon completion, the THF layer was separated. After removal of THF, the solid was washed with water and ethanol. The dried product was washed with acetone (**5** and **6**) or ethanol (**7** and **8**) using a Soxhlet apparatus for 24 h to remove the catalyst residues and oligomers. The polymers tended to form stable inclusion complexes with ethanol or acetone. Heating of the polymers at 120 °C under vacuum overnight removed the solvents. The products were isolated as light yellow powders.

Polymer 5. A light yellow solid. Anal. Calcd for $(C_{75}H_{80})_n$: C, 91.8%; H, 8.2%. Found: C, 91.2%; H, 8.2%. ^1H NMR (400 MHz, $CDCl_3$): δ 0.74 (br 12H), 1.03 (br 32 H), 1.99 (br, 8H), 7.10 (d, J = 8.4 Hz, 2H), 7.20 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 7.8 Hz, 4H), 7.42 (d, J = 8.4 Hz, 4H), 7.52−7.76 (m, 16 H). ^{13}C NMR (100 MHz, THF-d_8): δ 14.9, 24.0, 31.3, 33.1, 42.0, 55.6, 63.0, 121.1, 121.4, 121.8, 122.5, 124.2, 127.2, 127.6, 128.3, 132.4, 133.0, 134.2, 140.6, 141.0, 147.5, 152.3, 153.1.

Polymer 6. A light yellow solid. Anal. Calcd for $(C_{74}H_{80}Si)_n$: C, 89.1%; H, 8.1%. Found: C, 88.9%; H, 8.1%. ^1H NMR (THF-d_8): δ 0.67 (br, 12H), 0.97 (br, 32 H), 2.03 (br, 8H), 7.10−7.82 (m, 28 H). ^{13}C NMR (100 MHz, THF-d_8): δ 14.9, 24.0, 31.3, 33.0, 41.8, 56.0, 121.2, 121.6, 122.4, 122.8, 123.2, 126.7, 127.4, 127.7, 131.8, 134.5, 137.0, 138.2, 142.5, 152.5, 153.0.

Polymers 7 and 8. Light yellow solids. Anal. Calcd for $(C_{98}H_{96}Si)_n$: C, 90.4%; H, 7.4%. Found: C, 90.0%; H, 7.4%. ^1H NMR ($CDCl_3$): δ 0.77 (br, 12H), 1.09 (br, 32 H), 2.08 (br, 8H), 7.30 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H), 7.59−7.80 (m, 38 H). ^{13}C NMR ($CDCl_3$): δ 14.3, 22.9, 24.1, 30.1, 31.8, 40.8, 55.7, 120.1, 120.5, 121.8, 123.2, 126.3, 126.5, 127.1, 127.4, 127.8, 128.0, 129.0, 129.2, 132.3, 135.3, 139.9, 140.5, 141.1, 150.9, 151.8, 152.1.

EL Device Fabrication. For the fabrication of the devices, glass substrates coated with indium−tin oxide (ITO) with a sheet resistance of 30 Ω γ^{-1} (CSG Co. Ltd.) were cleaned sequentially in ultrasonic baths of aqueous ionic detergent, acetone, and anhydrous ethanol. A thin film layer of PEDOT (80 nm) and polymer **8** (50 nm) (from a 15 mg/mL solution of the polymers in THF solution) was spin-coated on the ITO surface at 1000 rpm for 60 s, after which a thin layer of LiF (0.5 nm)/Ca(20 nm) was deposited on the polymer film by thermal evaporation under a vacuum of 10^{-6} Torr. The active area of the device was about 4.0 mm^2. The applied dc bias voltages for EL devices were in a forward direction (ITO, positive; LiF/Ca/Ag, negative). The current−voltage characteristics were measured on a voltmeter and an amperometer, respectively. The EL efficiency and brightness measurements were carried out with a calibrated silicon photodiode. All the measurements of the EL devices were carried out in air at room temperature.

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