A Comparative Study on Luminescent Copolymers of Fluorene and Carbazole with Conjugated or δ-Si Interrupted Structures: Steric Effects

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ABSTRACT: Light-emitting alternating copolymers of 9,9-dialkylfluorene and *N*-hexylcarbazole with conjugated (**P1** and **P2**) and δ-Si interrupted (**P3** and **P4**) structures have been synthesized. The linear tetrahedral polymer **P3** and hyperbranched tetrahedral polymer **P4** were synthesized from two novel tetrahedral dibromo/tetrabromo precursors (**2** and **3**, respectively). The thermal and optical properties of all polymers in solution and the condensed state were investigated. A comparative study on the optical properties of **P1**−**P4** showed that, in the condensed state, **P1** and **P2** suffered seriously from concentration quenching (significant red shift in emission maximum, broadening in emission spectrum and tremendous decrease in quantum yield), whereas the two δ-Si interrupted **P3** and **P4**, particularly the latter, were tremendously less or not prone to self-aggregation such that they did not show significant concentration quenching in the condensed state. We represent in this paper an effective approach, a tetrahedral approach, for the synthesis of nonaggregating optoelectronic polymers.

Introduction

Over the past 20 years, studies on organic/polymeric light-emitting diodes (OLEDs/PLEDs) have drawn tremendous attention in industrial and academic research.[1] A major problem for LEDs is the aggregation-induced concentration quenching of luminescence of light-emitting polymers in the condensed state, which is particularly serious for red-light-emitting materials.[2] The aggregation-induced concentration quenching has also been identified as one of the major problems for polyfluorenes (PF), which is a class of the most studied light-emitting polymers.[3] From a chemical standpoint, this problem can be solved or alleviated by designing sterically hindered light-emitting materials. For example, studies on PFs containing bulky and oxidant-resistant groups at the 9-position,[4] cross-linked oligofluorene networks,[5] spirofluorene derivatives,[6] star-shaped,[7] ladder-type polyfluorenes,[8] and hyperbranched light-emitting polymers[9] have been reported. An attractive approach for the design of nonaggregating amorphous optoelectronic materials is to synthesize structurally “awkward”[10] tetrahedral materials from several precursors such as tetraphenylmethane and tetraphenylsilane.[11] Tetrahedral organic molecules and polymers containing δ-Si cores have been investigated as electroluminescent materials.[12] We have recently demonstrated that tetrahedral luminescent materials (small organic compounds and hyperbranched polymers) derived from several newly synthesized Si(p-Ar-Br)$_4$ precursors were not prone to self-aggregation in the solid state as evidenced by their close solution and film spectral similarities, as well as their high PL quantum efficiencies and low full width at half-maximum (fwhm) values of their emission spectra in film state.[13] Although it has been generally believed that the steric factor plays an important role on the optical properties of light-emitting materials in film state, no systematic and comparative studies on such steric effects have been reported. In this paper, we report the synthesis of two novel carbazole-based tetrahedral precursors, namely [di(3-bromo-*N*-hexylcarbazole-6-yl)-diphenyl]silane (**2**) and tetra(3-bromocarbazole-6-yl)silane (**3**), and the synthesis of their δ-Si interrupted linear and hyperbranched polymers with 9,9-dihexylfluorene-2,7-bis(trimethylene boronate) (**P3** and **P4**, respectively). We chose carbazole as a building unit because of its well-established hole-transporting ability,[12b,14] wide application as hosts in phosphorescent PLEDs,[15] and feasibility on tuning HOMO level by the N-substitutent.[15b] A comparative study on the optical properties of these two polymers with other two conjugated linear copolymers of *N*-hexylcarbazole and 9,9-dialkylfluorene (**P1** and **P2**) showed that, in the condensed state, **P1** and **P2** suffered seriously from concentration quenching (significant red shift in emission maximum, broadening in emission spectrum, and tremendous decrease in quantum yield), whereas the two δ-Si interrupted **P3** and **P4**, particularly the latter, were significantly less or not prone to self-aggregation such that they did not show significant concentration quenching in the condensed state.

Experimental Section

General Information. Unless stated otherwise, all reagents and solvents were of commercial grade and used as received. All reactions were performed under a purified nitrogen atmosphere using the standard Schlenk technique. 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 Bruker Autoflex TOF/TOF MALDI-TOF MS spectrometer using dithranol/Ag-TFA as a matrix. The molecular weights of polymers were determined by gel permeation chromatography (GPC, Waters) using polystyrenes as standards and THF as a mobile phase at 1.0 mL/min. UV−vis spectra were measured with a UV−vis spectrometer (Shimadzu, UV-2501 PC) at 25 °C. Fluorescence spectra were recorded on a LS50B luminescence spectrometer (Perkin-Elmer) at 25 °C. Glass transition temperatures were determined by differential scanning calorimetry (DSC) experi-

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ments 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. WAXS measurements were conducted using a Bruker X-ray diffractometer using Cu Kα (λ = 1.541 Å) radiation. Thin films of the samples prepared by a hydraulic press die were used for the measurements. 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.

The starting compounds *N*-hexyl-3,6-dibromocarbazole[16] and 9,9-dialkylfluorene-2,7-bis(trimethylene boronate)[17] were prepared according to the literature methods.

Synthesis of Compound 2. 3,6-Dibromo-*N*-hexylcarbazole (6 g, 7.3 mmol) was dissolved in dry THF (100 mL) and was cooled to −78 °C in an acetone/dry ice bath. To the solution was added *n*-BuLi (1.6 M, 6.0 mL, 1.1 equiv) dropwise via a syringe. The solution was stirred at −78 °C for 2 h and then was added dichlorodiphenylsilane (1.8 mL) in one portion. The reaction mixture was allowed to stir at −78 °C for 4 h and then was warmed to room temperature and stirred for 5 days. The reaction mixture was finally refluxed for 4 h. Upon completion, water was added (100 mL). The organic layer was isolated, and aqueous layer was extracted with dichloromethane (100 mL × 2). The combined organic solution was washed with water and dried ($MgSO_4$). The crude product was purified by column chromatography (hexanes/chloroform 2:1) to give the product as a white solid in 33% (2.03 g). Anal. Calcd for $C_{48}H_{48}Br_2N_2Si$: 840.82. C, 68.57; H, 5.75; N, 3.33; Br, 19.01. Found: C, 68.95; H, 6.18; N, 3.44; Br, 18.93. ^{1}H NMR ($CDCl_3$): δ 0.90 (t, $^3J_{H-H} = 6.8$ Hz, 6 H), 1.34 (m, 6 H), 1.40 (m, 6 H), 1.90 (m, 4 H), 4.30 (t, $^3J_{H-H} = 6.8$ Hz, 4 H), 7.31 (d, $^3J_{H-H} = 8.4$ Hz, 2H), 7.43−7.51 (m, 8H), 7.55 (d, $^3J_{H-H} = 8.4$ Hz, 2 H), 7.73 (dd, $^3J_{H-H} = 8.4$ Hz, $^4J_{H-H} = 1.6$ Hz, 4 H), 7.75 (d, $^3J_{H-H} = 8.8$ Hz, 2 H), 8.13 (s, 2 H), 8.32 (s, 2 H). ^{13}C NMR ($CDCl_3$): δ 14.3, 22.9, 27.3, 29.3, 31.9, 43.6, 109.1, 110.5, 112.2, 122.2, 123.5, 124.0, 124.9, 128.3, 128.6, 129.5, 129.8, 134.6, 135.8, 136.9, 139.5, 142.1. MALDI-TOF MS (*m*/*e*): 840.314 (M$^+$).

Synthesis of Compound 3. Compound **3** was synthesized similarly to **2**, except that $SiCl_4$ (0.25 equiv of 3,6-dibromo-*N*-hexylcarbazole) was used instead of $SiCl_2Ph_2$. **3** was obtained as a white solid in 30% yield (1.5 g). Anal. Calcd for $C_{72}H_{76}Br_4N_4Si$: 1345.13. C, 64.29; H, 5.70; Br, 23.76; N, 4.17. Found: C, 64.00; H, 5.33; Br, 23.69; N, 4.21. ^{1}H NMR ($CDCl_3$): δ 0.87 (t, $^3J_{H-H} =$ 6.8 Hz, 12 H), 1.31 (m, 16 H), 1.34 (m, 8 H), 1.87 (m, 8 H), 4.30 (t, $^3J_{H-H} = 6.8$ Hz, 8 H), 7.29 (d, $^3J_{H-H} = 8.8$ Hz, 4 H), 7.47 (d, $^3J_{H-H} = 8.0$ Hz, 4 H), 7.53 (dd, $^3J_{H-H} = 8.8$ Hz, $^4J_{H-H} = 2.0$ Hz, 4 H), 7.84 (d, $^3J_{H-H} = 8.0$ Hz, 4 H), 8.16 (d, $^4J_{H-H} = 2.0$ Hz, 4 H), 8.41 (s, 4 H). ^{13}C NMR ($CDCl_3$): δ 14.4, 22.9, 27.3, 29.3, 31.9, 43.6, 109.2, 110.5, 112.2, 122.2, 123.6, 124.4, 125.0, 128.6, 128.7, 133.6, 139.5, 142.3. MALDI-TOF MS (*m*/*z*): 1352.6 (M$^+$ + 7), 1374.4 (M$^+$ + Na$^+$), 1488.6 (M$^+$ + Ag$^+$).

Synthesis of Polymer P1 via Suzuki Coupling Method. *N*-Hexyl-3,6-dibromocarbazole (0.55 g, 1.34 mmol), 9,9-didodecylfluorene-2,7-bis(trimethylene boronate) (0.9 g, 1.34 mmol), and $[Pd(PPh_3)_4]$ (31 mg, 1 mol %) were dissolved in toluene (6 mL) and 2 M aqueous K_2CO_3 (4 mL). The reaction mixture was degassed by bubbling with N_2 for 15 min and then was heated at 90−100 °C for 2 days. Upon completion, the organic layer was separated and was washed with water and dried ($MgSO_4$). After removal of the organic solvent, the solid was continuously extracted with acetone for 48 h using a Soxhlet apparatus. (The catalyst residue, unreacted monomers, and low molecular weight oligomers were dissolved in acetone.) Polymer **P1** was obtained as a gray solid in 80% yield (0.8 g). Anal. Calcd for $(C_{55}H_{75}N)_n$: $(750.212)_n$. C, 88.06; H, 10.08; N, 1.87 C. Found: C, 88.22; H, 10.10; N, 1.39. ^{1}H NMR ($CDCl_3$): δ 0.82 (br, 6 H), 0.91 (br, 3 H), 1.16 (br, 40 H), 1.36 (br, 4 H), 1.46 (br, 2 H), 2.71 (br, 2 H), 2.14 (br, 4 H), 4.41 (br, 2 H), 7.53 (br, 2 H), 7.70−7.90 (m, br, 8 H), 8.52 (br, 2 H). ^{13}C NMR ($CDCl_3$): δ 14.4, 22.9, 23.0, 24.3, 27.4, 29.4, 29.7, 30.0, 30.5, 32.0, 32.2, 41.0, 43.6, 43.8, 55.7, 109.2, 109.4, 110.6, 114.3, 119.3, 120.2, 120.8, 122.0, 123.4, 123.8, 124.0, 125.7, 125.9, 126.1, 126.5, 127.5, 129.1, 133.4, 139.9, 140.3, 140.8, 141.2, 152.0.

Polymer P2. The polymer was previously synthesized from *N*-hexyl-3,6-dibromocarbazole and 9,9-dihexyl-2,7-dibromofluorene using Ni(0)-catalyzed polymerization reaction, but no characterization data were given.[18] In the present work, **P2** was synthesized from *N*-hexyl-3,6-dibromocarbazole and 9,9-dihexylfluorene-2,7-bis(trimethylene boronate) according to the method for **P1** and was obtained as a gray solid in 92% yield (2.6 g). Anal. Calcd for $(C_{43}H_{51}N)_n$: $(581.888)_n$. C, 88.76; H, 8.83; N, 2.41. Found: C, 88.32; H, 8.67; N, 2.68. ^{1}H NMR ($CDCl_3$): δ 0.83 (br, 6 H), 0.93 (br, 3 H), 1.16 (br, 12 H), 1.38 (br, 4 H), 1.48 (br, 2 H), 1.98 (br, 2 H), 2.19 (br, 4 H), 2.14 (br, 4 H), 4.42 (br, 2 H), 7.56 (br, 2 H), 7.78 (br, 4 H), 7.87 (br, 4 H), 8.54 (br, 2 H). ^{13}C NMR ($CDCl_3$): δ 14.5, 23.0, 24.3, 27.5, 29.5, 30.2, 32.0, 32.1, 41.1, 43.8, 55.8, 109.3, 109.5, 119.4, 120.0, 120.3, 122.1, 123.3, 123.7, 123.9, 124.1, 125.7, 126.0, 126.2, 126.6, 127.2, 127.6, 129.2, 133.5, 140.0, 140.8, 141.3, 141.5, 152.1.

Polymer P3 was synthesized similarly from *N*-hexyl-3,6-dibromocarbazole and precursor **2** and was obtained as a gray solid in 90% yield (0.85 g). Anal. Calcd for $(C_{73}H_{80}N_2Si)_n$: $(1013.543)_n$. C, 86.51; H, 7.96; N, 2.76. Found: C, 86.54; H, 7.85; N, 3.07. ^{1}H NMR ($CDCl_3$): δ 0.75 (m, 6 H), 0.91 (br, 6 H), 1.07 (br, 12 H), 1.36 (br, 12 H), 1.47 (br, 4 H), 1.96 (br, 4 H), 2.10 (br, 4 H), 4.37 (br, 4 H), 7.41−7.58 (m, br, 6 H), 7.67−7.69 (br, 2 H), 7.74−7.87 (br, m, 6 H), 8.35 (br, 2 H), 8.55 (br, 2 H). ^{13}C NMR ($CDCl_3$): δ 14.33, 14.37, 22.9, 24.1, 27.4, 29.4, 30.0, 31.8, 31.9, 40.9, 43.6, 55.7, 109.0, 109.2, 119.4, 120.1, 122.0, 123.4, 123.6, 123.7, 125.8, 126.5, 128.2, 129.4, 129.7, 133.6, 134.3, 136.3, 137.0, 139.8, 140.3, 141.1, 142.3, 152.0.

Synthesis of Polymer P4. Tetrabromo precursor **3** (0.4 g, 0.3 mmol), 9,9-dihexylfluorene-2,7-bis(trimethylene boronate) (0.3 g, 0.6 mmol), and $[Pd(PPh_3)_4]$ (14 mg, 1 mol %) were dissolved in toluene (20 mL) and 2 M aqueous K_2CO_3 (14 mL). The reaction mixture was degassed by bubbling with N_2 for 15 min and then was heated at 90−100 °C for 2 days. Upon completion, the organic layer was separated and was washed with water and dried ($MgSO_4$). After removal of the organic solvent, the solid was continuously extracted with acetone for 48 h using a Soxhlet apparatus. (The catalyst residue, unreacted monomers, and low molecular weight oligomers were dissolved in acetone.) The remaining solid residue was then extracted with THF for 24 h. The THF solution was concentrated to give the soluble polymer **5** as a yellow solid in 38% yield (0.2 g).[13e] Anal. Calcd for $(C_{122}H_{140}N_4Si{\cdot}4H_2O)_n$: $(1762.636)_n$. C, 83.13; H, 8.46; N, 3.18. Found: C, 83.22; H, 8.66; N, 3.38; Br, 1.92 (from residual end groups). ^{1}H NMR ($CDCl_3$): δ 0.72 (br, 12 H), 0.87 (br, 12 H), 1.03 (br, 32 H), 1.32 (br, 24 H), 1.93 (br, 8 H), 2.05 (br, 8 H), 4.36 (br, 8 H), 7.50 (br, 12 H), 7.65 (br, 20 H), 7.79 (br, 4 H), 7.86 (br, 4 H), 8.41 (br, 4 H), 8.70 (br, 4 H). ^{13}C NMR ($CDCl_3$): δ 14.4, 21.5, 22.9, 24.1, 27.3, 29.4, 30.0, 30.7, 31.8, 31.9, 34.6, 40.8, 43.6, 55.6, 109.0, 109.2, 119.4, 120.1, 121.9, 123.2, 123.5, 123.8, 124.3, 125.9, 126.4, 127.0, 127.2, 128.6, 129.2, 133.4, 136.2, 139.8, 140.3, 141.0, 142.6, 152.0.

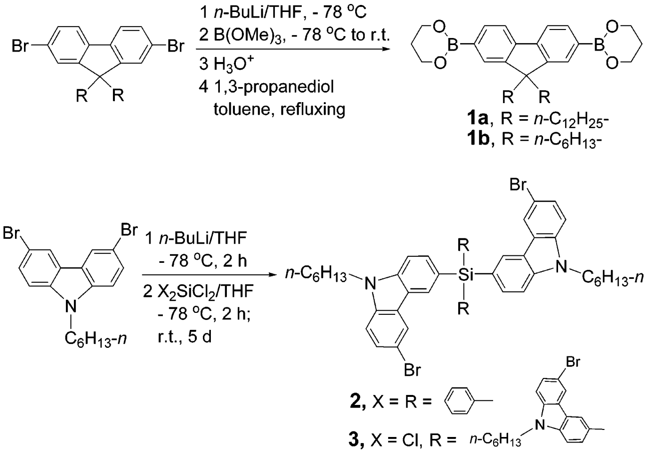
Quantum Yield Determination. The relative photoluminescent quantum yields (Φ_{PL}) of the compounds in THF were determined using a solution of quinine sulfate as a standard (ca. 1 × 10^{-5} M in 0.1 M H_2SO_4, having a quantum yield of 55%). Dilute sample solutions were used for the determinations (absorbance < 0.1). All samples were degassed before measurements. The correction of emission spectra was carried out by reference to quinine bisulfate in acidic solution (400−600 nm) according to the literature method.[19] 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%). Thin films (absorbance < 0.2) were dried at 50 °C under a vacuum oven for 16 h before measurements. Values are calculated according to eq 1, where Φ_{unk} is the fluorescence quantum yield of the sample, Φ_{std} is the fluorescence quantum yield of the standard, I_{unk} and I_{std} are the integrated emission intensities of the sample and the standard, respectively, A_{unk} and A_{std} are the absorbances of the sample and the standard at the excitation wavelength, respec-

Table 1. Synthesis, Thermal, and Optical Properties of Precursors 2 and 3[a]

				UV		PL (nm)		
	yield (%)	T_g (°C)[b]	T_d (°C)[c]	λ_{max} (nm)	log ϵ	$\lambda_{max,em}$[d]	fwhm	$\lambda_{max,ex}$[e]
2	33	63	412	276, 304, 340, 356	4.91, 4.49, 3.86, 3.86	379	54	331
3	30	65	434	278, 304, 340, 356	5.18, 4.78, 4.20, 4.20	379	47	330

[a] Sample concentrations for **2** and **3** were at ca. 1 × 10^{-5} M. [b] The middle temperatures. [c] T_d is defined as the temperature at which a 5% weight loss is recorded by the TGA analysis. [d] The excitation wavelength was 304 nm. [e] The emission wavelengths were 379 nm. em = emission; ex = excitation.

Scheme 1. Synthesis of the Starting Compounds 1−3



tively, and η_{unk} and η_{std} are the refractive indexes of the corresponding solutions (pure solvents were assumed).[20]

$$\Phi_{unk} = \Phi_{std}(I_{unk}/A_{unk})(A_{std}/I_{std})(\eta_{unk}/\eta_{std})^2 \qquad (1)$$

Results and Discussion

The synthesis of the starting materials **1**−**3** is shown in Scheme 1. The syntheses of the two tetrahedral precursors **2** and **3** were achieved by monolithiation of *N*-hexyl-3,6-dibromocarbazole with *n*-butyllithium at −78 °C similarly to a literature method[21] and subsequent substitution between the monolithiate and Ph_2SiCl_2 and $SiCl_4$, respectively. Compounds **2** and **3** were obtained as white solids in moderate yields. The structures of these precursors were fully characterized by ^{1}H and ^{13}C NMR, MALDI-TOF MS spectroscopy, and elemental analysis. For example, the ^{13}C NMR spectra of **2** and **3** exhibited 16 and 12 discrete aromatic-*C* peaks, respectively, as expected. Table 1 summarizes their synthesis, thermal, and optical properties. Both compounds are amorphous in nature with obvious glass transition temperatures (T_g) of 63 and 65 °C, respectively. The glassy natures of **2** and **3** were further confirmed by their wide-angle X-ray diffraction (WAXD) patterns, which showed a similar profile with a same amorphous peak around $2\theta = 20°$. **2** and **3** exhibit high thermal stability with decomposition temperature (T_d) being over 400 °C. The UV and photoluminescence properties of **2** and **3** in THF are recorded (Figure 1). The UV spectra of **2** and **3** exhibit a similar pattern with strong absorptions at ca. 278 and 304 nm and relatively weaker absorptions at 340 and 356 nm. The former two peaks are from $\pi \rightarrow \pi^*$ excitations of the carbazole arms, whereas the latter can be attributed to a hyperconjugation via the central δ-Si atom[22] and was also observed previously in the UV spectrum of tetra(2-bromofluorene-7-yl)silane.[13d] It is noteworthy that **3** exhibits significantly stronger absorptions than **2**, indicating stronger constructive excitonic coupling among the four arms.[22] The excitation spectra of **2** and **3** are structureless, with excitation maxima at ca. 330 nm. Moreover, the excitation spectrum of **3** exhibits a broad peak ranging from 310 to 340 nm, perhaps due to complex excitonic couplings among the four arms. Compounds **2** and **3** emitted violet-blue light in THF solution with a same emission maximum of 378 nm.

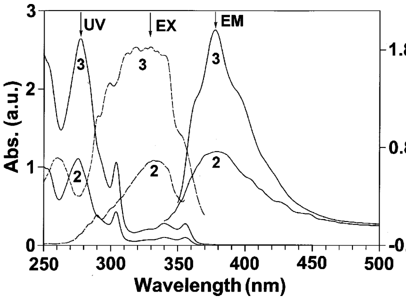
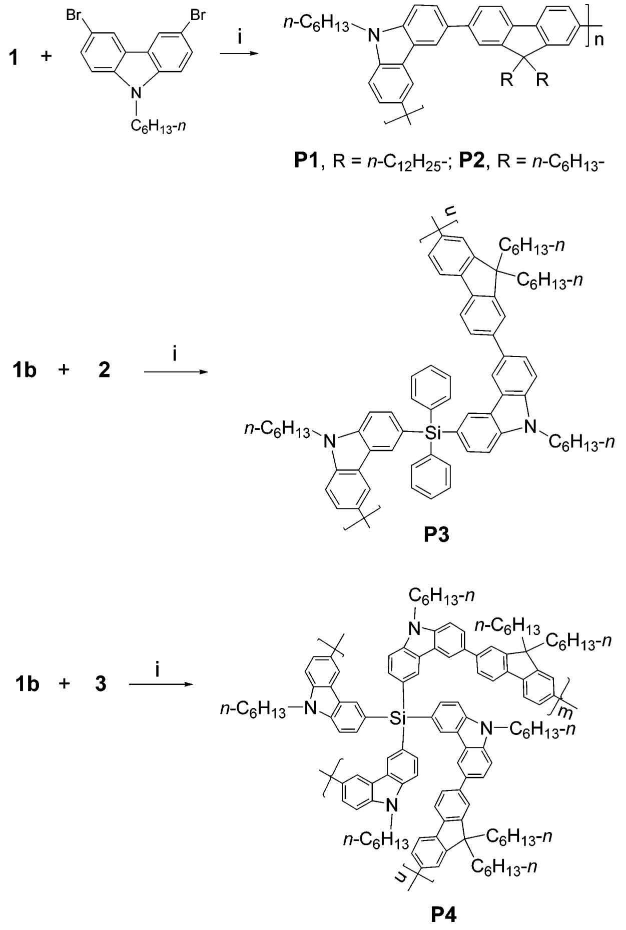


Figure 1. UV and PL emission and excitation spectra of **2** and **3** in THF solutions.

Scheme 2. Synthesis of Polymers P1−P4[a]



[a] i = [Pd(PPh$_3$)$_4$], toluene/2 M K_2CO_3, 90−100 °C, 2 days.

Scheme 2 shows the synthesis of polymers **P1**−**P4** via the Suzuki coupling method. A summary of their synthesis, thermal, and optical properties is given in Table 2. It should be pointed out that some conjugated polymers with similar structures to **P1** and **P2** have been synthesized previously by the Suzuki

Table 2. Thermal and Optical Properties of Polymers P1−P4[a]

				UV/THF	EM/THF			UV/film	EM/film		
	M_w (PD)[b]	T_g (°C)	T_d (°C)	λ_{max} (nm)	λ_{max}[c]	fwhm	Φ_{PL}[d]	λ_{max} (nm)	λ_{max}[c]	fwhm	Φ_{PL}[d]
P1	11870 (1.7)	67	424	349	402, 415	54	0.42	346	478	131	*f*
P2	14950 (1.7)	153	436	350	400, 416	51	0.69	346	459	96	0.08
P3	15070 (1.7)	154	440	307, 347	413, 401[e]	57	0.86	308, 347	441	100	0.52
P4	17570 (1.3)	131	325	307, 346	413, 438[e]	56	0.66	307, 347	413, 435[e]	55	0.59

[a] Sample concentrations were at ca. 4.0 × 10^{-3} g/L. [b] By GPC in THF (polystyrene calibration). It should be noted that the polystyrene calibration often underestimate the molecular weight of hyperbranched polymers.[26] [c] The excitation wavelength was their respective long wavelength absorption maximum. [d] The relative photoluminescence quantum yields (Φ_{PL}) of the compounds 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 of 1 × 10^{-3} M and a quantum efficiency of 83%) as a standard. [e] Shoulder peaks. [f] <8.0 × 10^{-3}.

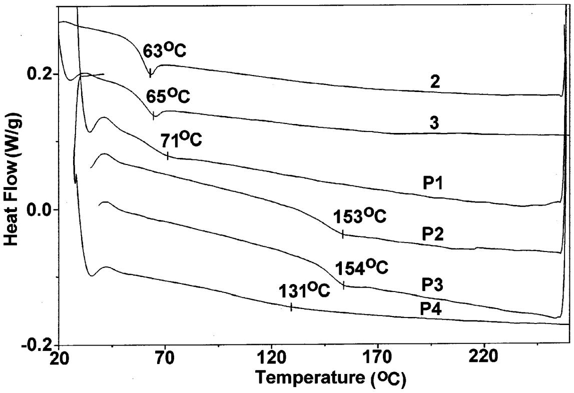


Figure 2. DSC thermograms of precursors and polymers measured under nitrogen at a heating rate of 10 °C/min (recorded during the second heating scan).

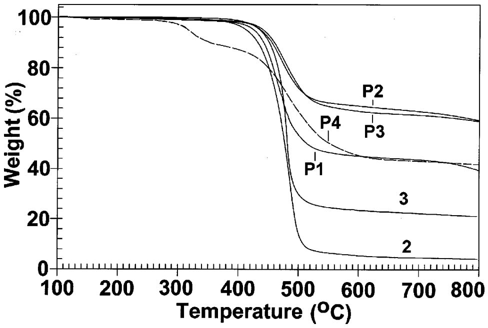


Figure 3. TGA thermograms of precursors and polymers. The thermal analyses were carried out under nitrogen at a heating rate of 20 °C/min.

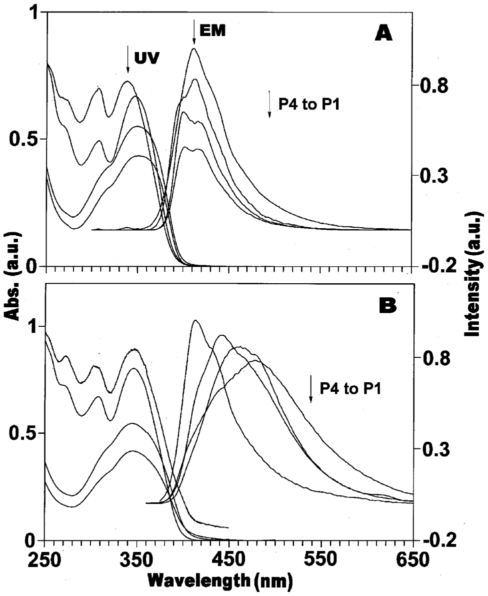


Figure 4. UV and emission spectra of **P1**−**P4** in THF solution (A) and the spin-coated film state (B).

Table 3. Band Gaps (E_g/eV[a]) of Polymers P1−P4 in Solution and Film State

	P1	P2	P3	P4
in solution	2.87	3.01	2.99	3.00
in film state	2.82	2.82	3.01	2.82

[a] The band gaps were estimated from their respective onset wavelengths of UV spectra in solution and film state; $E_g = E_{LUMO} - E_{HOMO}$.

coupling method[16,23] and Yamamoto coupling method.[18,24] For the synthesis of the hyperbranched polymer **P4**, reaction was carried out in dilute solution to minimize the formation of cross-linked insoluble polymer. The polymers were purified by continuous extraction with acetone using a Soxhlet apparatus. The polymers have comparable molecular weights with M_w in the range of 11 800−17 600 and relatively narrow distributions. It is noteworthy that all the four polymers should have residual bromo and boronate end groups, as no further end-capping reactions were carried out. All the four polymers were well soluble in common organic solvents such as dichloromethane, chloroform, THF, and toluene but not soluble in ethanol and acetone. The structures of **P1**−**P4** were satisfactorily characterized by ^{1}H and ^{13}C NMR spectroscopy and elemental analysis. The thermal properties of **P1**−**P4** were investigated by DSC and TGA studies (Figures 2 and 3). Except that **P1** exhibits a low T_g (67 °C) due to the long alkyl chains at C-9 of fluorene, the other three polymers exhibit high T_gs (>130 °C). All three linear polymers **P1**−**P3** also show high T_ds (>400 °C), whereas the hyperbranched **P4** showed the lowest T_d (325 °C), and no weight losses are recorded at lower temperatures. It is important to note that high T_g and T_d are important for an optoelectronic polymer to be used for practical PLED applications.[25]

The UV and PL properties of **P1**−**P4** in THF solution and the film state were investigated (Figure 4, Table 2). Uniform transparent thin films were prepared on quartz substrates by spin-coating from toluene solutions of **P1**−**P4** (about 2 wt %) at a spin rate of 1000 rpm and were dried under vacuum at 50 °C for 16 h. The band gaps of **P1**−**P4** are estimated from their respective onset wavelength of UV spectrum and are in the range of 2.87−3.01 eV (THF solution) and 2.82−3.01 eV (film state) which are typical for deep blue to blue emissions (Table 3). In dilute THF solution, both the conjugated **P1** and **P2** show similar UV and PL emission spectral patterns with similar absorption and emission maxima at ca. 350 and 400 nm and PL quantum efficiencies of 42% and 69%, respectively. The absorption and emission maxima of **P1** and **P2** are very similar to those of an analogous copolymer containing octyl groups at the N- and C-9 positions of carbazole and fluorene, respectively.[27] The quantum yields of **P2** and the reference polymer[27] are almost the same. All these results show that the length of the C-9 alkyl chain in fluorene does not have significant effects on the optical properties of the carbazole−fluorene copolymers, which is consistent with previously reported results.[28] In the film state, the absorption maxima of **P1** and **P2** are slightly blue-shifted from those of their solution ones. However, their emission maxima are tremendously red-shifted by 76 and 59 nm, respectively. There are also significant broadenings in their emission spectra (fwhm values increases by 77 and 45 nm, respectively). Most notably, the PL quantum efficiencies of **P1** and **P2** decrease tremendously to <0.8% and 8%, respectively. All these results reveal that concentration quenching happened in the film state of **P1** and **P2.** It is noteworthy that **P1** suffered more seriously from concentration quenching than **P2** did, which can be attributed to a higher tendency of self-aggregation of **P1** in the film state, due to stronger hydrophobic−hydrophobic interactions among the longer C-9 alkyl chains. In THF solution, the two tetrahedral polymers **P3** and **P4** show similar UV spectra with similar absorption maxima at ca. 307 and 346 nm. **P3** and **P4** exhibit the same emission maximum at 413 nm, with similar fwhm values of ca. 56 nm and comparable PL quantum yields of 86% and 66%, respectively. Some other linear poly(*p*-phenylenevinylene)-related copolymers with a uniform π-conjugated segment regulated by δ-Si units have been reported previously.[12a−c,29] It has been demonstrated that incorporation of nonconjugated spacer silicon units into polymer rigid backbone can render this class of luminescent polymers unique characteristics and functionality such as better solubility/processability in organic solvents, limited conjugation length, and more exactly predictable PL properties.[12c] The δ-Si interrupted linear polymer **P3** indeed showed better solubility in various organic solvents than the conjugated counterparts. **P3** generally showed higher T_g, T_d, and PL quantum efficiency than the analogous Si-containing PPV-related linear polymer;[12a−c,29] perhaps due to its more rigid structure and the presence of more efficient fluorene units. In the film state, the absorption maxima of **P3** and **P4** are not significantly different from their solution ones. The emission maximum and fwhm of **P3** increase by 28 and 43 nm from solution values, respectively. The film quantum yield of **P3** decreases marginally to 52%. For the hyperbranched **P4**, its film emission spectrum is essentially the same as its solution one, with almost the same emission maximum and fwhm being recorded, although its quantum efficiency decreases slightly to 59%.

The above optical data of **P1**−**P4** show that (1) in dilute THF solution, all the four polymers behaved similarly with similar absorption and emission maxima and comparable PL quantum efficiencies, and (2) in the condensed state, the two fully conjugated polymers behaved tremendously differently from the two δ-Si interrupted polymers, with the former suffered seriously from concentration quenching while the latter did not. That polymers **P1**−**P4** have similar absorption and emission maxima in solution indicates that the effective conjugation lengths of the two conjugated polymers **P1** and **P2** are similar to those of the δ-Si interrupted polymers **P3** and **P4**, which only have six conjugated phenyl rings in one chromophore unit. This is due to the fact that the incorporation of 3,6-carbazole units into the fluorene polymer interrupts the linear conjugated structures of the polymers.[24a] In the condensed state, the serious concentration quenching of **P1** and **P2** is due to their more planar structures and π−π and hydrophobic−hydrophobic interactions-driven self-aggregation. Concentration quenching of the δ-Si interrupted linear polymer **P3** in the condensed state was significantly less serious than those of **P1** and **P2**, as its film PL quantum efficiency is comparable to its solution one. The hyperbranched polymer **P4** did not show significant concentration quenching in the film state, which is evidenced by the close similarities in solution and film UV and PL emission spectra as well as its high film PL quantum yield and low fwhm. Recently, some hyperbranched luminescent polyarylenes have been synthesized by cobalt- and tantalum-catalyzed polycyclotrimerizations and tungsten-catalyzed metathesis polymerizations.[30] These hyperbranched polymers generally showed very high thermal stability and high PL quantum efficiencies.[30a,b,f] It has also been reported that some hyperbranched polyarylenes were efficient UV emitters (Φ_{PL} up to 0.98) and excellent optical limiters.[30e] These hyperbranched polyarylenes were demonstrated not prone to aggregation in the solid thin film state as revealed by similarity between solution and thin film PL emission maxima, which is consistent with our present findings.[30c] We have previously demonstrated that the quantum confinement effect existed in some bulk eight-armed organic clusters comprising an oligosilsequioxane (POSS) octahedral core when the length of chromophoric arms is smaller than the exciton Bohr radii ($a_B \approx 1.2-2$ nm). As such, the exciton is confined and difficult to jump to the neighboring arms, which in turn lead to higher quantum efficiency. On the other hand, if the confinement effect is low, the exciton may move to neighboring chain easily and trapped in defects, which would lead to low quantum efficiency.[31] Modeling studies showed that the sizes of the isolated chromophore units in **P3** and **P4** were less than 1.4 nm. We anticipate that the remarkable photoluminescence properties of **P3** and **P4** in the film state are partially due to the quantum confinement effect arising from small sizes of their isolated chromophores and three-dimensional hindered structures. As polymers **P2**−**P4** have the same hexyl substituents at N- and C-9 positions and comparable molecular weights, their differences in PL behaviors in the condensed state can be attributed to their steric structures. With the increase in steric hindrance from fully conjugated linear planar structure to δ-Si interrupted linear tetrahedral structure and to δ-Si interrupted hyperbranched structure, concentration quenching decreases dramatically. We thus conclude that interruption of the conjugation of carbazole−fluorene copolymer by δ-Si does not have significant effects on their UV and emission maxima and quantum efficiency in solution but can significantly reduce or even eliminate the aggregation-induced concentration quenching in the solid state. This finding is important as it is possible to design luminescent polymers with nonconjugated junctions (i.e., δ-Si spacer), which have high PL quantum efficiencies in both solution and film state and are less or even not prone to self-aggregation in condensed state due to their steric junctions. One important feature for such polymers is that they can be made with high molecular weight yet still have better solubility in organic solvents and thus are more solution processable than fully conjugated polymers.[12]

We present in this paper an effective approach, a tetrahedral approach, for the synthesis of nonaggregating optoelectronic polymers. Two δ-Si interrupted blue-light-emitting polymers, a linear polymer **P3** and a hyperbranched polymer **P4**, were synthesized. Both **P3** and **P4** showed high thermal stability (high T_g and T_d) and were not or significantly less prone to self-aggregation and concentration quenching in the film state. It is important to note that the linear polymer **P3** had better solubility in organic solvents than the hyperbranched polymer **P4**, indicating that **P3** should have better solution processability than **P4**. Thus, although **P4** showed better PL properties in the condensed state, the linear polymer **P3** might be preferred in terms of device application due to its better solution processability. We are currently carrying out a comparative study on the electrochemical properties of the carbazole-containing polymers and applying the two tetrahedral polymers for PLEDs. Studies on novel green- and red-light-emitting hyperbranched polymers using this tetrahedral approach are also in progress.

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Supporting Information Available: ^{1}H NMR, ^{13}C NMR, and MALDT-TOF MS spectra of **2** and **3** and ^{1}H and ^{13}C NMR spectra of **P1−P4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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