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# Novel Glassy Tetra(*N*-alkyl-3-bromocarbazole-6-yl)silanes as Building Blocks for Efficient and Nonaggregating Blue-Light-Emitting Tetrahedral Materials

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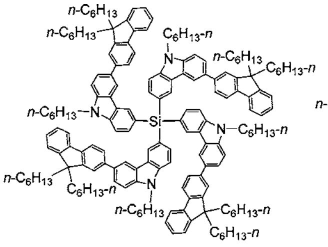
## ABSTRACT



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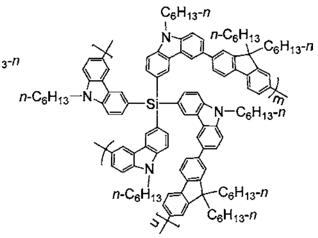

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**Tetrahedral precursors of tetra(*N*-alkyl-3-bromocarbazole-6-yl)silanes (1–3), which were amorphous with $T_g$ being adjustable by changing the chain length of the N-substitutent, were developed. Fluorene-conjugated glassy compound 4 and hyperbranched polymer 5 were synthesized from the precursors via Suzuki coupling reaction. 4 and 5 emitted blue light efficiently in the condensed state with high quantum efficiencies of 80 (4) and 59% (5) and small fwhm (full width at half-maximum) of 48 (4) and 55 nm (5), indicating that they did not pack into detrimental aggregates in the solid state.**

During the past 20 years, fluorene-based polymers and oligomers (PFs) have been intensively investigated as blue-light-emitting materials for organic/polymeric light-emitting diodes (OLEDs/PLEDs) due to their high photo- and electroluminescence efficiency and excellent chemical and thermal stabilities.[1] Recent efforts on PFs have been focused on solving their self-aggregation problem in the condensed state, which resulted in red-shifted and less efficient emission and reduced color purity, qualities that would hamper practical applications of PFs in LEDs.[2] It has been well established that PFs with hindered structures are less prone to self-aggregation in the film state.[3] One attractive approach for the design of nonaggregating amorphous optoelectronic materials is to synthesize structurally "awkward"[4] tetrahedral organic compounds from several precursors such as tetraphenylmethane and tetraphenylsilane.[5] Such awkward structures can render these compounds amorphous in nature and make it difficult for them to pack into detrimental aggregates in the film state.[6] Indeed, Si-based tetrahedral organic molecules and polymers have been intensively investigated as electroluminescent materials.[7] We have recently reported a series of tetrahedral luminescent materials comprising $CPh_4$[8] and $SiAr_4$ cores.[9] We found that their fluorene derivatives were efficient blue-light-emitting materials and that Si-centered materials were superior with regard to film-

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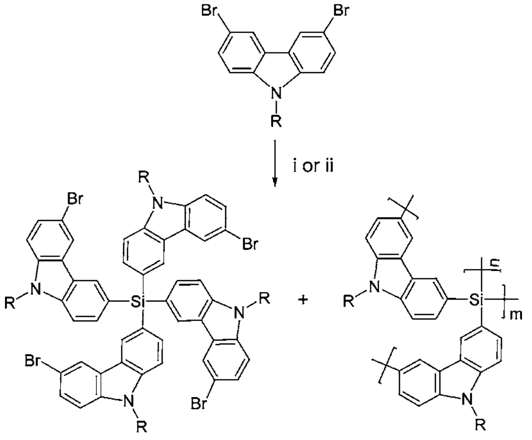
forming ability and quantum efficiency.[9] Two noteworthy features of Si-centered tetrahedral materials are their high PL efficiency (nearly 100%[9b]) and small fwhm values (as low as 45 nm[10] ) in the condensed state. Such features are due to the quantum confinement effects arising from their small sizes (less than 2 nm, which is close to exciton Bohr radii ($a_B$)) and three-dimensional hindered structures.[11] In a continuation on our research on tetrahedral luminescent materials, we herein report the development of novel glassy tetrabromocarbazolylsilane precursors with tunable glass transition temperatures ($T_g$s) and their use as building blocks for blue-light-emitting materials. We chose carbazoles as building units because of their well-established hole-transporting ability,[12] wide application as hosts in phosphorescent PLEDs,[13] and feasibility of tuning the HOMO level by changing the N-substitutent.[13b]

Scheme 1 shows the synthetic routes to precursors **1**−**3**. A summary of the synthesis and thermal and optical properties is given in Table S1 (Supporting Information). We first tried to synthesize **1**−**3** via the Grignard route,[8,9] which involved a reaction between *N*-alkyl-3,6-dibromocarbazole and Mg (1.2 equiv) to form a mono Grignard reagent, and subsequent substitution reaction between the Grignard reagent and $Si(OMe)_4$. Silica gel column chromatography of the crude products, however, afforded **1**−**3** in less than 10% yields. To identify the major reaction pathway of these reactions, the residues in the column were washed out by ethyl acetate after separation of **1**−**3** and were further purified by continuous extraction with acetone for 24 h using a Soxhlet apparatus to give polymers **P1**−**P3** in around 40% yields. The molecular weights ($M_w$s) of **P1**−**P3** were in the range of 3800−8000 (GPC, THF, polystyrene standards). **P1**−**P3** were the major products in these Grignard reactions. Hence, a considerable amount of *N*-alkyl-3,6-dibromocarbazole has undergone reaction with Mg to form BrMg−Ar−MgBr under the reaction conditions. The formations of **P1**−**P3** involve polycondensation reactions between the $AB_4$-type monomer $Si(OMe)_4$ and a $AB_2$-type monomer BrMg−Ar−MgBr, and most likely **P1**−**P3** have hyperbranched structures.[9,10] To improve the yields of precursors **1**−**3**, we tried to prepare them via the lithiation route using *n*-BuLi (1.2 equiv) at −78 °C.[14] It should be noted that lithiation of Ar−Br by *n*-BuLi at a higher temperature (i.e., 0 °C) tended to give an Ar−Bu-*n* byproduct.[15] Subsequent reaction of Li−Ar−Br with $Si(OMe)_4$ afforded **1**−**3** in much improved yields (>40%). In contrast, the polymeric byproducts were obtained in < 10% yields. The chemical structures of **1**−**3** were characterized by NMR and MALDI-TOF MS spectroscopy and elemental analysis. For example, the $^1$H NMR spectra of **1**−**3** in $CDCl_3$ exhibit a similar pattern in the aromatic region with four doublets and two singlets at $\delta$ 7.29−7.30 (d, 4 H), 7.46−7.47 (d, 4 H), 7.52−7.53 (d, 4 H), 7.84−7.86 (d, 4 H), 8.15−8.17 (s, 4 H), 8.40−8.41 (s, 4 H).

**Scheme 1.** Synthesis of Precursors **1**−**3**[a]



**1**, R = Et
**2**, R = *n*-Bu
**3**, R = *n*-hexyl

**P1**, R = Et
**P2**, R = *n*-Bu
**P3**, R = *n*-hexyl

[a] Key: (i) (a) Mg/THF, refluxing, 16 h; (b) $Si(OMe)_4$, rt, 2 days, refluxing for 4 h; (c) 1 N HCl, 0.5 h. (ii) (a) *n*-BuLi/THF, −78 °C, 4 h; (b) $Si(OMe)_4$, −78 °C, 4 h, rt, 5 days, refluxing for 4 h; (c) 1 N HCl, 0.5 h.

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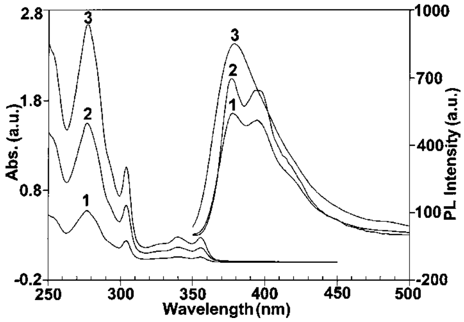
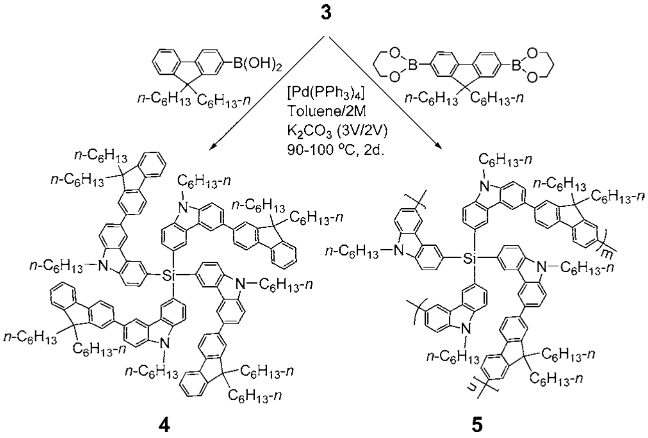


**Figure 1.** UV and PL emission spectra of **1**−**3** in THF.

The UV and PL emission spectra of **1**−**3** in dilute THF solutions were recorded (Figure 1 and Table S1). The N-substituent does not show significant effects on the optical properties of **1**−**3**. The UV spectra of **1**−**3** exhibit strong absorptions around 278 and 304, 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 may be attributed to a hyperconjugation via the central $\delta$-Si atom[16] and was also observed in the UV spectrum of tetra(2-bromofluorene-7-yl)silane.[10] Compounds **1**−**3** emitted violet-blue light in THF solution. The PL emission spectra of **1** and **2** exhibit a similar pattern with two peaks around 378 and 394 nm. The PL emission spectrum of **3** exhibits a structureless pattern with an emission maximum at 379 nm, which is perhaps due to its more crowded structure relative to **1** and **2**. The PL emission spectra of **1**−**3** are narrow with small fwhm values of only 46−49 nm. The UV spectra of **P1**−**P3** in THF show similar patterns and absorption peaks to those of **1**−**3**; however, their PL emissions become structureless with significantly red-shifted emission maxima. The red shifts in emission maxima and broadenings of emission spectra of **P1**−**P3** can be attributed to a higher tendency for them to self-aggregate in solution than their small tetrahedral analogues. The thermal properties of **1**−**3** and **P1**−**P3** were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) (Figure S1 and Table S1, Supporting Information). Compounds **1**−**3** exhibit obvious glass transitions with $T_g$ at 65−137 °C, indicating their amorphous natures. The glassy natures of **1**−**3** were further confirmed by their wide-angle X-ray diffraction (WAXD) patterns, which showed a similar profile with the same amorphous peak around $2\theta = 20°$. The $T_g$ of **1**−**3** decreases with the increase in chain length of N-substitutent, which reveals that the $T_g$s of the precursors can be tuned simply by N-substitutent. The thermal stability of **1**−**3**, however, increases with increases in the chain length of the N-substitutent, with the decomposition temperature ($T_d$) of **3** being the highest (434 °C). Polymers **P1**−**P3** show high $T_g$s and $T_d$s, but their dependences on N-substitutent are not as significant as those of **1**−**3**.

Syntheses of the two blue-light-emitting compounds **4** and **5** were achieved by Suzuki coupling reaction (Scheme 2).

**Scheme 2.** Synthesis of Two Blue-Light-Emitting Materials by the Suzuki Coupling Method



Compound **4** was obtained as a white solid in 60% yield. For the synthesis of the hyperbranched polymer **5**, reaction was carried out in a dilute toluene/$K_2CO_3$ (aq) solution (monomer concentrations were in 0.015 and 0.030 M, respectively) to minimize the formation of cross-linked insoluble polymer. Polymer **5** was obtained as a yellow solid in 38% yield after purification by a two-step continuous Soxhlet extraction, where first acetone was used to remove catalyst residue, unreacted monomers, and small oligomers, followed by use of THF to extract soluble **5**. In addition, the reaction also produced about 10% insoluble polymer network. Polymer **5** had a $M_w$ of 17 570 ($M_w/M_n = 1.3$, GPC) and was well soluble in chloroform, THF, and toluene but insoluble in acetone and ethanol. The $^1$H NMR spectrum of **4** in $CDCl_3$ exhibits two low-field singlets at $\delta$ 8.40 and 8.68 (Ar-*H* from carbazole) and two triplets at $\delta$ 4.36 (N$CH_2$ of carbazole, 8H) and 2.00 (C$CH_2$ of fluorene, 16 H). The MALDI-TOF MS spectrum of **4** shows a molecular ion peak at 2355 ($M^+$). The $^1$H NMR spectrum of **5** in $CDCl_3$ exhibits two broad peaks at $\delta$ 4.36 (N$CH_2$ from carbazole units) and 2.05 (C$CH_2$ from fluorene units) at a ratio of 1:1 corresponding to monomer feed. Compound **4** shows a $T_g$ of 78 °C, which is significantly higher than that of **3**. The $T_g$ of **5** is recorded at 131 °C. **4** and **5** are thermally stable, with $T_d$s of 426 and 325 °C, respectively.

The UV and PL properties of **4** and **5** in THF solution and in the film state were investigated (Figure 2, Table 1). Uniform transparent thin films were prepared on quartz substrates by spin coating from toluene solutions of **4** and **5** (about 2 wt %) at a spin rate of 1000 rpm and dried under a vacuum at 50 °C for 16 h. The UV spectra of **4** and **5** in THF show two long-wavelength peaks at 307, 326 and 307, 346 with tailing to 380 and 420 nm, respectively, which are from the $\pi \rightarrow \pi^*$ excitations of the chromophoric arms. A significant red shift in the longer wavelength absorption maximum of **5** relative to that of **4** is due to a longer chromophoric arm in **5** (carbazole-fluorene-carbazole vs

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**Table 1.** Summary of Thermal and Optical Properties of **4** and **5**[a]

| | | | absorption (solution) | | emission (solution)[b] | | absorption (film) | emission (film)[b] | |
|---|---|---|---|---|---|---|---|---|---|
| | $T_g$ (°C) | $T_d$ (°C) | $\lambda_{max}$ (nm) | log $\epsilon_{max}$ | $\lambda_{max}$ (nm) (fwhm/nm) | $\phi_{PL}$[c] (%) | $\lambda_{max}$ (nm) | $\lambda_{max}$ (nm) (fwhm/nm) | $\phi_{PL}$[c] %) |
| **4** | 78 | 426 | 307, 326 | 5.26, 5.24 | 377, 395 (43) | 0.75 | 309, 330 | 399, 382[d] (48) | 0.80 |
| **5** | 131 | 325 | 307, 346 | | 413, 438[d] (56) | 0.66 | 307, 347 | 413, 435[d] (55) | 0.59 |

[a] Sample concentrations were $3.47 \times 10^{-6}$ M for **4** and $2.8 \times 10^{-3}$ g/L for **5**. [b] Excitation wavelengths were 307−309 nm. [c] Photoluminescence quantum yields ($\Phi_{PL}$) of the compounds in THF were determined using a solution of quinine sulfate (ca. $1 \times 10^{-5}$ M in 0.1 M $H_2SO_4$, having a quantum yield of 55%) as a standard. The $\Phi_{PL}$ values of films were determined using 9,10-diphenylanthracene (dispersed in PMMA films with a concentration of $1 \times 10^{-3}$ M and a quantum efficiency of 83%) as a standard. [d] Shoulder peaks.

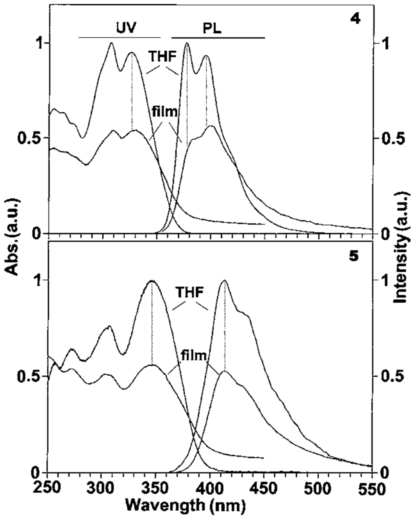

**Figure 2.** UV and PL emission spectra of **4** and **5** in a THF solution and in the spin-coated film state.

carbazole-fluorene). Compound **4** emitted intense violet-blue light peaking at 377 and 399 nm, with a small fwhm of only 43 nm and a $\phi_{PL}$ of 75%. Polymer **5** emitted strong blue light peaking at 413, with a small fwhm of 56 nm and a $\phi_{PL}$ of 66%. The emission maximum of **5** is also significantly red shifted from that of **4** due to a longer conjugation length. Furthermore, both the absorption and emission maxima of **5** are significantly red shifted from those of the carbazole-fluorene-carbazole oligomer (corresponds to the chromophoric arm in **5**, which has absorption and emission maxima at 318 and 401 nm, respectively[17]), indicating constructive coupling among chromophore units in **5**. The changes in absorption and emission maxima of **4** in the film state are not significant except that the longer absorption (326 nm) and emission (395 nm) peaks become stronger. The fwhm of the film emission spectrum of **4** increases slightly to 48 nm, but its quantum efficiency reaches 80%. In the film state, polymer **5** exhibits essentially the same UV and PL emission spectra as those in THF solution with slightly reduced quantum yield. All these results show that aggregation-induced concentration quenching does not happen in the condensed state of **4** and **5**. It is of importance to note that **4** performs better than **5** with regard to quantum efficiency and color purity (smaller fwhm), although it contains only a short carbazole-fluorene chromophore. We anticipate that the remarkable photoluminescence property of **4** is due to the quantum confinement effect arising from its small size and three-dimensionally hindered structure.

In summary, we have developed a facile and effective method for the synthesis of novel carbazole-based Si(Ar−Br)$_4$ precursors, which are amorphous in nature with $T_g$ being adjustable by changing the chain length of the N-substitutent. A glassy compound **4** and a hyperbranched polymer **5** were synthesized from the precursors and boronates of 9,9-dihexylfluorene via a one-step Suzuki coupling reaction. These two materials did not pack into detrimental aggregates in the condensed state as evidenced by their close spectral similarities in the solution and film state, as well as their high PL efficiencies and low fwhm values. These novel blue-emitters were solution processable and exhibited good film-forming ability, high thermal stability, and possibly good hole-transporting ability.

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**Supporting Information Available:** Experimental procedures, all characterization data and spectroscopic information of new compounds and polymers, DSC and TGA thermograms of **1**−**5**, and UV and PL emission spectra of **P1**−**P3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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