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Communication

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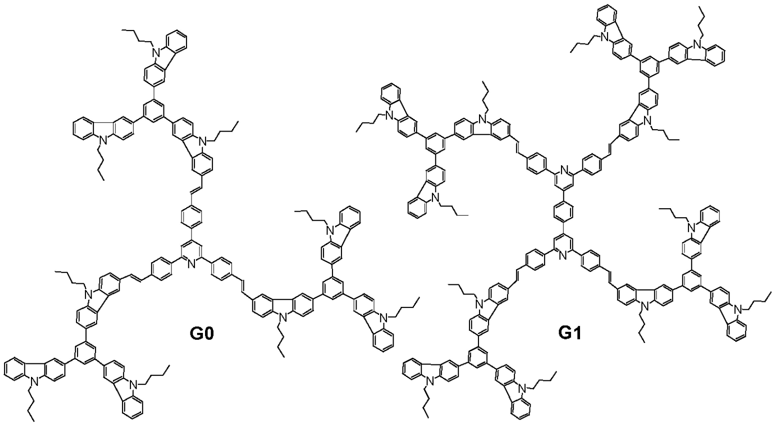

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A Facile Synthesis and Properties of Multicarbazole Molecules Containing Multiple Vinylene Bridges

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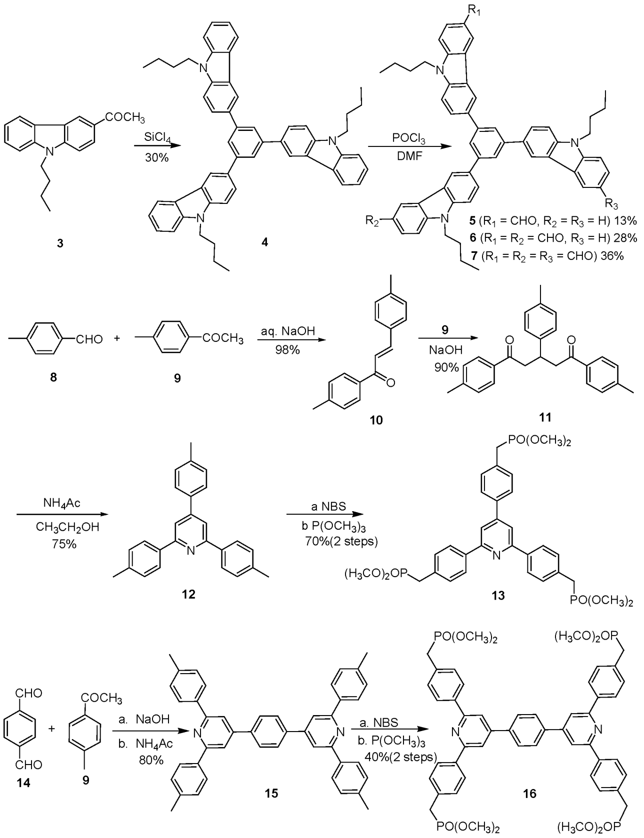
In the past several decades, linear π-conjugated organic molecules and polymers have been studied extensively not only for fundamental interest but also for their many promising applications, such as for organic light-emitting diodes (OLEDs), nonlinear optical properties, conductivity, photocells, field-effect transistors (FETs), and so on, due to their delocalized π systems.[1] A challenge in this area is to achieve light-emitting materials with long-term stability and high efficiency. However, linear conjugated molecules tend to aggregate because of $\pi-\pi$ stacking interactions, which act as energy traps and hence lead to increased nonradiative decay. In addition, their electronic properties and solubility cannot be tuned independently, which is a disadvantage for comprehensive optimization of these materials. Recently multibranched π-conjugated materials and hyperbranched polymers have received considerable interest in both academic research and industrial applications because of their unusual molecular structures and increasing potential as active components for a wide range of electronic and optoelectronic devices.[2] Moreover, because of their highly branched and well-defined structures, such materials are expected to be less aggregated and, hence, should not suffer from fluorescence quenching due to intermolecular interaction. Therefore, their optical properties, especially the quantum yields of light emission, can be fine-tuned via appropriate choice of the fluorescent core.[4]

Carbazole is a conjugated unit that has interesting optical and electronic properties such as photoconductivity and photorefractivity. A number of carbazole derivatives have been designed and synthesized.[3] Organic electronic devices, such as OLEDs, based on these derivatives have been investigated. Carbazole derivatives are often used as the materials for hole-transporting layers, utilizing the high charge mobility.[4] Carbazole derivatives are also used as light-emitting layers because they are thermally stable and show blue photo- and electroluminescence due to the large bang gap of the biphenyl unit and planarity improved by the bridging nitrogen atom.

Our basic idea in this communication is to introduce carbazole into a branched structure to combine the multifunctional properties of carbazole and hyperbranched compounds. To realize this purpose, we present a facile method for preparation of two novel π-conjugated multibranched compounds of 1,3,5-tri(*N*-(*n*-butyl)-3-carbazolyl)benzene through multiple vinylene bridges, **G0** and **G1**, which contain, respectively, up to nine and 12 carbazole units with good yields. These branched compounds have good solubility and intermediate molecular size (about 5 nm). The relationships of their structures and optical properties have been investigated.

The syntheses of the key **G0** and **G1** are shown in Scheme 1. Our synthesis started with the cheap carbazole **1**, which was easily converted to 3-acetyl-9-(*n*-butyl)carbazole **3** by N-alkylation and Friedel−Crafts reactions. 1,3,5-Tri(*N*-(*n*-butyl)-3-carbazolyl)benzene **4** was synthesized by condensation of three molecules **3** with 30% yield in the presence of $SiCl_4$, which was similar to previously reported ones.[5] Vilsmeier formylation of **4** in $POCl_3$/DMF obtained **5**, **6**, and **7**, respectively. It was noteworthy that the most effective method to convert **8** and **9** into **10** with nearly 100% yield was under 2% NaOH aqueous phase condition. The Michael addition reactions carried out smoothly under solvent-free procedures afforded **11** with a good yield (90%), and then the diketone **11** was treated with ammonium acetate in ethanol to generate **12** in 75% yield. **15** was readily accessible via sequential solventless aldol condensation and Michael addition involving NaOH, followed by treatment with ammonium acetate in ethanol, as a one-pot reaction with yield of 80%.[6] The compounds **13** and **16** were synthesized from **12** and **15** with 70 and 40% overall yield in a two-step sequence based on an NBS bromination and a Michaelis−Arbuzov reaction, respectively.

Scheme 1



The synthetic approach to **G0** and **G1** is outlined in Schemes 1 and 2. Wittig−Horner−Emmons reaction was alternatively utilized to construct a vinylene linkage. It is well-known that the Wittig or Wittig−Horner−Emmons reaction is one of the most powerful and useful reactions utilized in the construction of carbon−carbon double bond. The Wittig reactions were carried out under a few

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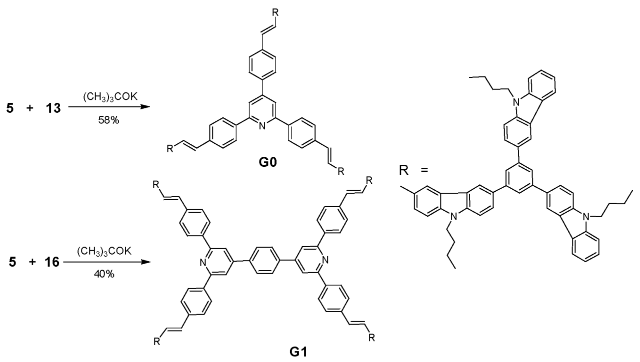
Scheme 2



reaction systems, such as NaOH/CH_3OH, C_2H_5OLi/C_2H_5OH, C_2H_5ONa/C_2H_5OH, $(CH_3)_3COK$/THF, $(CH_3)_3COK$/$(CH_3)_3COH$, $(CH_3)_3COK$/DMF, NaH/THF, and NaOH. Recently, a limited number of reports have appeared on Wittig olefination in solventless systems.[7] Synthetically considering reaction conditions, reagents, purification processes, and yields, we selected the room-temperature solid-phase reaction as the optimal synthesis route. It is noteworthy that Wittig−Horner−Emmons condensations of aldehyde **5** with **13** or **16** and fresh $(CH_3)_3COK$ placed in a dry mortar and manually milled for 10 min afforded fluorophores **G0** and **G1** in solvent-free and room-temperature conditions in good yield (**G0** 58.1%; **G1** 40%), respectively. Undoubtedly, the procedure is applicable to an even wider range.

All intermediates and the multibranch compounds **G0** and **G1** were characterized by a combination of IR, NMR, and matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectroscopy. MALDI-TOF mass spectroscopy is most valuable for higher molecular weight compounds (MW > 1500) where other methods become less applicable because diagnostic NMR signals become difficult to discern due to the growing intensities of the signals corresponding to the interior and periphery of the dendrons. We employed MALDI-TOF/MS measurements to characterize the precise structure, the molecular weight. The results are shown in Figures S2 and S3. The compounds are readily soluble in common organic solvents, such as CH_2Cl_2, chloroform, THF, toluene, and DMF.

The photophysical properties of **4**, **G0**, and **G1** were examined by UV−vis and fluorescence spectroscopy in THF solution and thin films on quartz plates. The spectra are shown in Figure 1. Normally, π-conjugated multibranches show a very strong $\pi-\pi^*$ electron absorption band in the UV−visible region, which progressively red-shifts with an increase of the effective conjugated length and numbers of branches. From absorption spectra in Figure 1a in THF solutions, we observed that absorption λ_{max} values (302 nm for **G0** and 295 nm for **G1**) exhibit a similar λ_{max} with the increase of the carbazole moieties in comparison with that of **4** (292 nm). However, absorption spectra show very strong broad absorption bands from 310 to 420 nm for **G0** and **G1**. Moreover, there are obviously red-shifts from **4** to **G0** and **G1** in absorption spectra. The absorption λ_{max} for these compounds might belong to $\pi-\pi^*$ electron absorption band of cross-conjugation. However, from **G0** to **G1**, the number of branching increases resulted in only a change in the intensities, and probably the cross-conjugation effect is relatively unimportant. As Figure 1 shows, the absorption spectra of solutions and corresponding films are nearly identical. But the PL peak wavelengths of **G0** and **G1** in film states are apparently red-shifted to those in THF solutions.

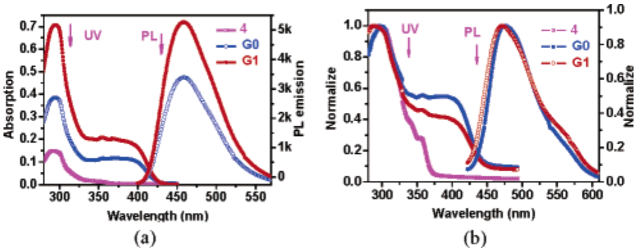


Figure 1. Absorption and PL spectra (a) in THF solution and (b) in film state.

In conclusion, we have presented a facile approach for the synthesis of a family of large-size and π-conjugated multibranch compounds exhibiting strong bluish-green fluorescence as potential candidates for OLEDs by molecular designs. The double bonds in the multibranched compounds are formed by solvent-free Wittig−Horner−Emmons reactions. The reaction conditions are mild, and the processes are simple and can tolerate a large variety of functional groups. We believe that this approach will be applicable for the construction of other structurally uniform and well-defined π-conjugated functional multibranched compounds. The details on the OLEDs performance using these materials as hole transfer and emitting layers or as host materials for electrophosphorescent applications will be reported in the future.

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Supporting Information Available: Experimental procedures and all characterization data of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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