Synthesis and Characterization of Monodendrons Based on 9-Phenylcarbazole

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A series of 9-phenylcarbazole ethynylene monodenrons have been prepared by palladium-catalyzed coupling reactions creating well-organized arrays of redox centers. The *tert*-butyl groups attached to the 3,6-positions of peripheral 9-phenylcarbazole monomers provide adequate solubility to a limited degree. Trimer and 7-mer monodendrons were prepared using a monomer with 3,3-diethyltriazene at its focal point. To facilitate purification, the synthesis of 15-mer monodendron, however, required a monomer bearing a 3-hydroxy-3-methyl-but-1-ynyl group at its focal point as a masking group for the terminal acetylene functionality. Although the solubility was limited, high generation monodendrons were found to be readily soluble in carbon disulfide, a solvent of high polarizability. Spectroscopic studies showed that there is limited through-bond conjugation over the monodendrons, but fluorescence studies suggested the presence of long-range through-space interactions in the higher members of the series.

Introduction

The organization of chromophores plays essential roles in controlling fundamental photolytic processes such as light absorption, energy transfer (exciton diffusion), photoinduced charge generation, and charge transfer.[1,2] These effects are relevant in a variety of interesting applications such as artificial photosynthesis, thin-film transistors, photovoltaic cells, electroluminescent materials, and photorefractive materials. Both covalent and noncovalent strategies have been exploited in the construction of spatially well-defined chromophore arrays.[2] Examples of noncovalent systems include micelles and reverse micelles, Langmuir–Blodgett films, liquid crystals, lipid bilayers, and multilayer thin films.[3,4] Noncovalent systems can involve large numbers of chromophores and be easily extended into macroscopic dimensions. However, these systems afford less precise control over chromophore organization than covalent systems.[5] Through covalent synthesis, chromophores can be accurately positioned over dimensions up to 10 nm within a single molecule. Studies on these systems will help elucidate the basic structural parameters controlling the energy and electron flow in molecular systems.

Chromophore arrays based on linear systems are simple, usually easy to synthesize, and have been extensively studied.[5−9] However, linear chain molecules can usually afford control in only one dimension. To realize more compact arrangements characterized by higher dimensions, chromophores can be incorporated into a well-defined dendritic structure. Rigid dendritic macromolecules can provide a suitable framework for such constructions. There have already been many photophysical studies involving dendritic macromolecules as scaffolding for building chromophore arrays.[10−12] In most cases, however, the photoactive unit has been incorporated either as a single core[12−16] or as peripheral groups[10,17−19] rather than as the dendritic repeating unit.

Carbazole has strong absorption in the near-UV region and a low redox potential. The electrochemical and spectroscopic properties of carbazole and its derivatives have been extensively studied.[20−22] Chemically, carbazole can be easily functionalized at its 3-, 6-, or 9-positions and covalently linked to other molecular moieties.[23] As a result of its special photo, electrical, and chemical properties, carbazole has been used as a functional building block in the fabrication of organic photoconduc-

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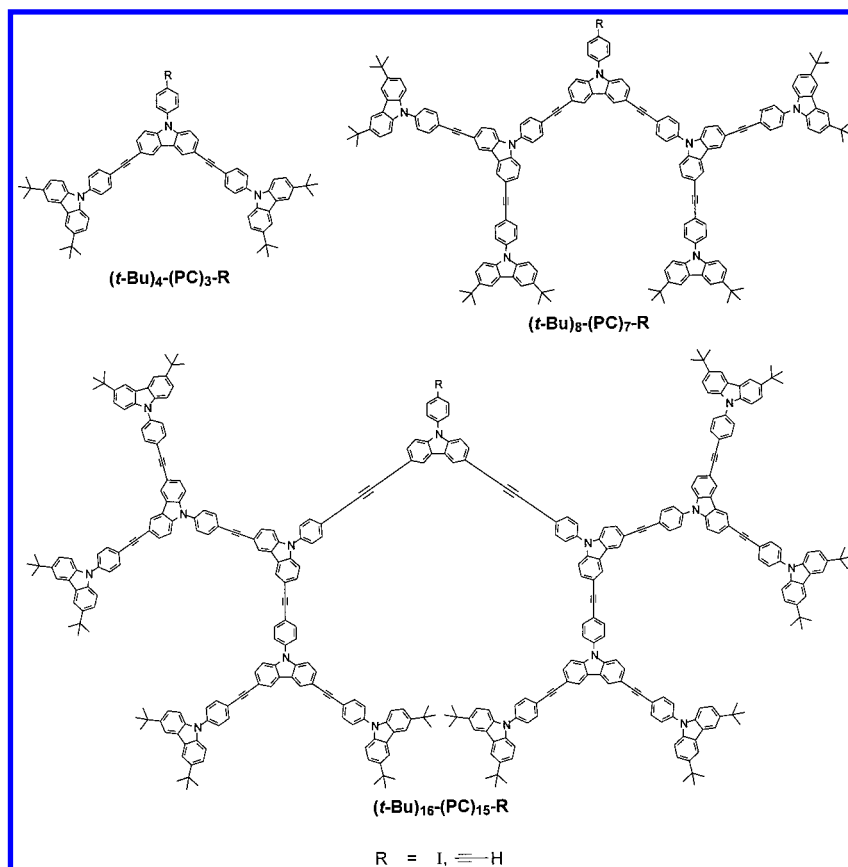
Figure 1. 9-Phenylcarbazole monodendrons with *tert*-butyl groups at the periphery.

tors, NLO materials, and photorefractive materials.[24-26] Poly(vinylcarbazole), a well-known photoconductor, has been used as the hole-transport component in the construction of several photo- and electroluminescent devices and photorefractive materials.[27-29] Here we describe the preparation of a series of well-defined dendrimers based on 9-phenylcarbazole as the fundamental building block.

Results and Discussion

In phenylacetylene dendrimer synthesis,[30-33] 3,5-di-*tert*-butyl-phenyl peripheral groups were successfully used to maintain the solubility of the dendrimers. Using this approach, dendrimers with molecular weights up to 40 kDa have been realized.[34] Following this lead, 9-(4-iodo-phenyl)-carbazole with two *tert*-butyl groups at the 3,6-positions of carbazole was chosen as the peripheral

monomer. The *tert*-butyl groups are expected to increase the solubility of the dendrimers and provide stability to the carbazole in its oxidized form.[20,21] The structures of 9-phenylcarbazole dendrimers that will be discussed are shown in Figure 1. Because of the rigid nature of the arylacetylene linkage, the relative positions of the 9-phenylcarbazole units are spatially controlled over dimensions up to ca. 50 Å, based on a molecular model of the 15-mer monodendron. These dendrimers should be suitable for the study of electronic communication between redox centers.

The most efficient synthesis of phenylacetylene dendrimers has involved a monomer with a triazene group at the focal point and two or more acetylene groups branching from the monomer.[34] The triazene group can be transformed to an aryl iodide[35] that can undergo subsequent coupling reactions. As an extension of this approach, a 9-phenylcarbazole derivative with a diethyltriazene group at the 4-position of the phenyl ring and two acetylene groups at the 3,6-positions of carbazole was chosen as the initial monomer. However, because of the difficulty in dendrimer purification caused by the self-coupling between terminal acetylenes, as well as side reactions associated with the transformation of triazenes to iodides, this monomer worked well only for the synthesis of the first two generations of monodendron. A different focal point monomer containing a polar masking group for the terminal acetylene functionality was then designed and synthesized to realize a 15-mer monodendron.

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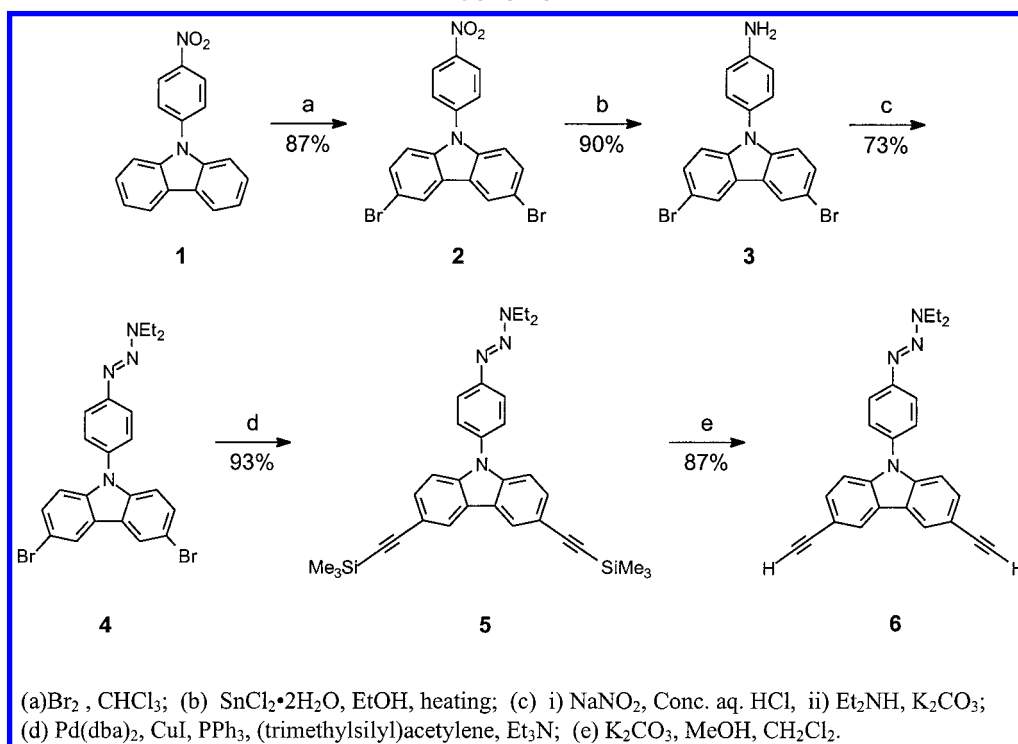(31) Xu, Z.; Moore, J. S. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 246–248.

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Scheme 1

(a) Br$_2$, CHCl$_3$; (b) SnCl$_2$·2H$_2$O, EtOH, heating; (c) i) NaNO$_2$, Conc. aq. HCl, ii) Et$_2$NH, K$_2$CO$_3$; (d) Pd(dba)$_2$, CuI, PPh$_3$, (trimethylsilyl)acetylene, Et$_3$N; (e) K$_2$CO$_3$, MeOH, CH$_2$Cl$_2$.

Monomer Synthesis. The synthesis of the monomer, 3,6-diethynyl-9-(4-(3,3-diethyltriazenyl)-phenyl)-carbazole (**6**) is outlined in Scheme 1. Following a literature procedure,[36] commercially available carbazole was fused with potassium hydroxide at about 350 °C, and the resulting potassium carbazole salt was treated with nitrobenzene to give 9-(4-nitrophenyl)-carbazole (**1**). Compound **1** was purified by crystallization from benzene after steam distillation of excess nitrobenzene. Treatment of **1** with 2 equiv of bromine gave 3,6-dibromo-9-(4-nitrophenyl)-carbazole (**2**) in good yield. Reduction of **2** with stannous chloride in refluxing ethanol gave 3,6-dibromo-9-(4-aminophenyl)-carbazole (**3**), which was converted to the corresponding diazonium salt and treated with diethylamine to give 3,6-dibromo-9-(4-(3,3-diethyltriazenyl)-phenyl)-carbazole (**4**). Sonogashira coupling of **4** with trimethylsilylacetylene gave 3,6-bis(trimethylsilylethynyl)-9-(4-(3,3-diethyltriazenyl)-phenyl)-carbazole (**5**) in good yield. The trimethylsilyl groups were removed by the treatment of **5** with potassium carbonate in a mixed solvent of methanol and dichloromethane to give the desired monomer 3,6-diethynyl-9-(4-(3,3-diethyltriazenyl)-phenyl)-carbazole (**6**). The reactions in the sequence could be easily carried out on a large scale (up to 40 g) without complication. The overall yield of **6** was 46%.

The synthesis of the peripheral monomer, 3,6-di-*tert*-butyl-9-(4-iodo-phenyl)-carbazole is illustrated in Scheme 2. Friedel−Crafts alkylation of 9-(4-nitrophenyl)-carbazole (**1**) with *tert*-butyl chloride in the presence of aluminum chloride gave 3,6-di-*tert*-butyl-9-(4-nitrophenyl)-carbazole (**7**), which was reduced to 3,6-di-*tert*-butyl-9-(4-aminophenyl)-carbazole (**8**). Amine **8** was converted to the corresponding diazonium salt, which was treated with diethylamine to give 3,6-di-*tert*-butyl-9-(4-(3,3-diethyltriazenyl)-phenyl)-carbazole (**9**). Triazene **9** was heated with methyl iodide at 110 °C in a sealed tube to afford the iodide **10**. Compounds **7** and **8** were easily

purified by recrystallization, and compounds **9** and **10** were purified by flash chromatography followed by recrystallization. The overall yield from **1** to **10** was ca. 60%.

Convergent Synthesis of the Monodendrons. As shown in Scheme 3, the monodendrons were prepared by alternatively repeating the coupling reaction and the transformation of the triazene to the corresponding iodo group. Heating (*t*-Bu)$_4$(PC)$_3$N$_3$Et$_2$ (**11**) with methyl iodide at 110 °C for 14 h afforded (*t*-Bu)$_4$(PC)$_3$I (**12**) in good yield. However, when (*t*-Bu)$_8$(PC)$_7$N$_3$Et$_2$ (**13**) was subjected to the same condition, a large amount of unknown byproducts that proved difficult to separate was obtained. To avoid this complication, a modified procedure (methyl iodide, iodine, 80 °C)[37] was used. Under these conditions, higher yields and cleaner products were obtained.
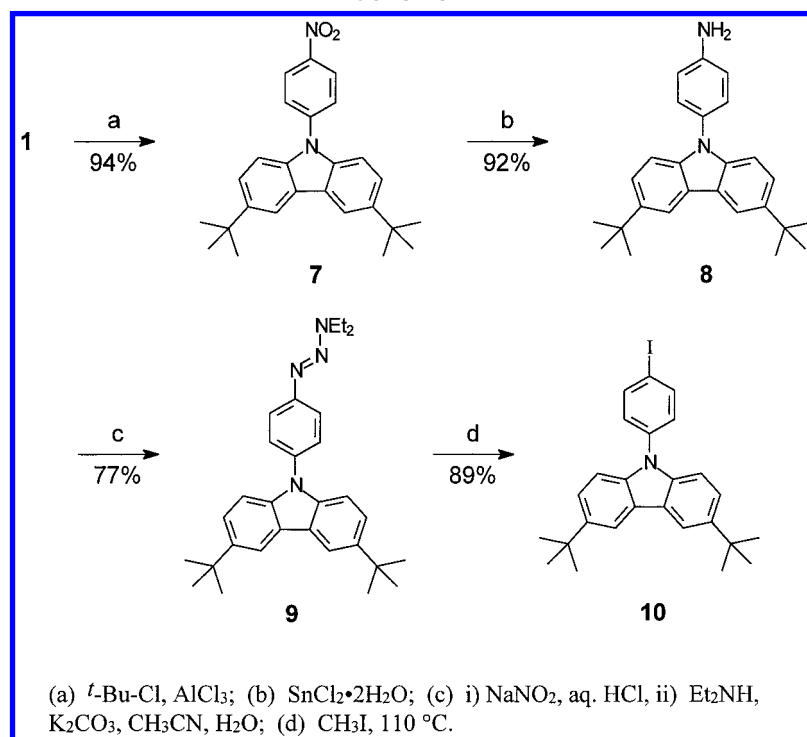
The approach shown in Scheme 3 worked well for the preparation of the first two generations of monodendrons. Both triazene and iodo functionalized first and second generations can be obtained in good yield and high purity, as verified by HPLC. However, it proved very difficult to synthesize higher generations of monodendron by this approach. One possible problem is the oxidative dimerization of monomer **6** to form diacetylene byproducts. This problem was also encountered in the synthesis of phenylacetylene dendrimers.[31] Gel permeation chromatogram of the reaction mixture of (*t*-Bu)$_8$(PC)$_7$I (**14**) with monomer **6** showed a significant amount of high molecular weight byproducts. Because of the poor solubility of high generations of monodendrons, these impurities were very difficult to remove by adsorption chromatography.

To overcome the self-coupling problem and facilitate product purification, another monomer (**22**, Scheme 4) was synthesized. This monomer has a 3-hydroxy-3-
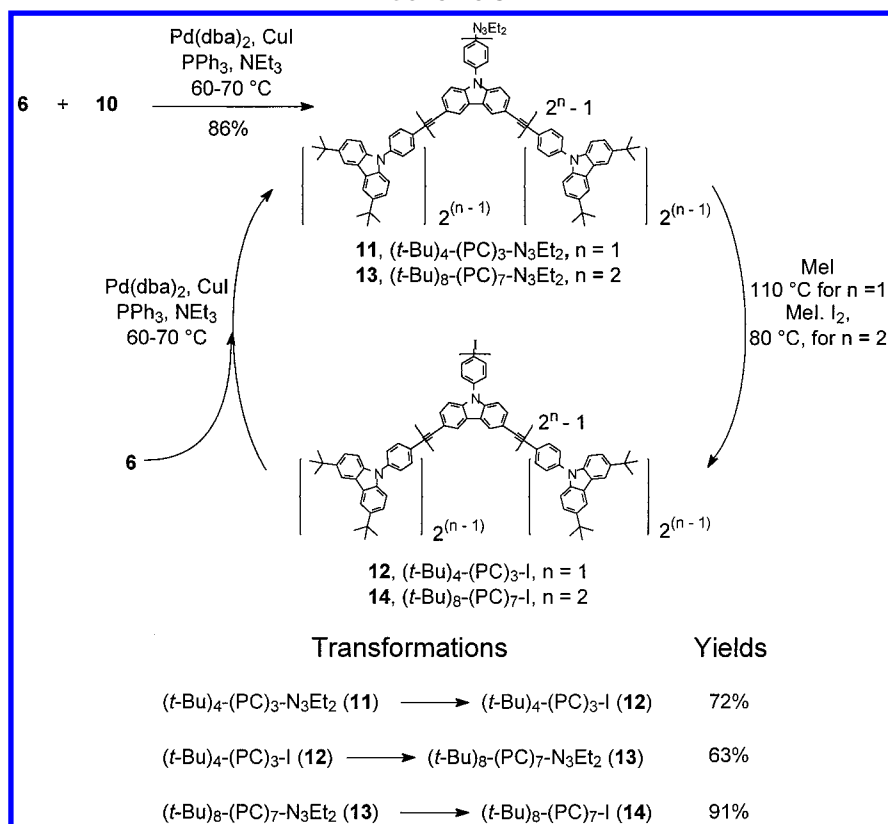
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Scheme 2

(a) *t*-Bu-Cl, AlCl$_3$; (b) SnCl$_2$•2H$_2$O; (c) i) NaNO$_2$, aq. HCl, ii) Et$_2$NH, K$_2$CO$_3$, CH$_3$CN, H$_2$O; (d) CH$_3$I, 110 °C.

Scheme 3

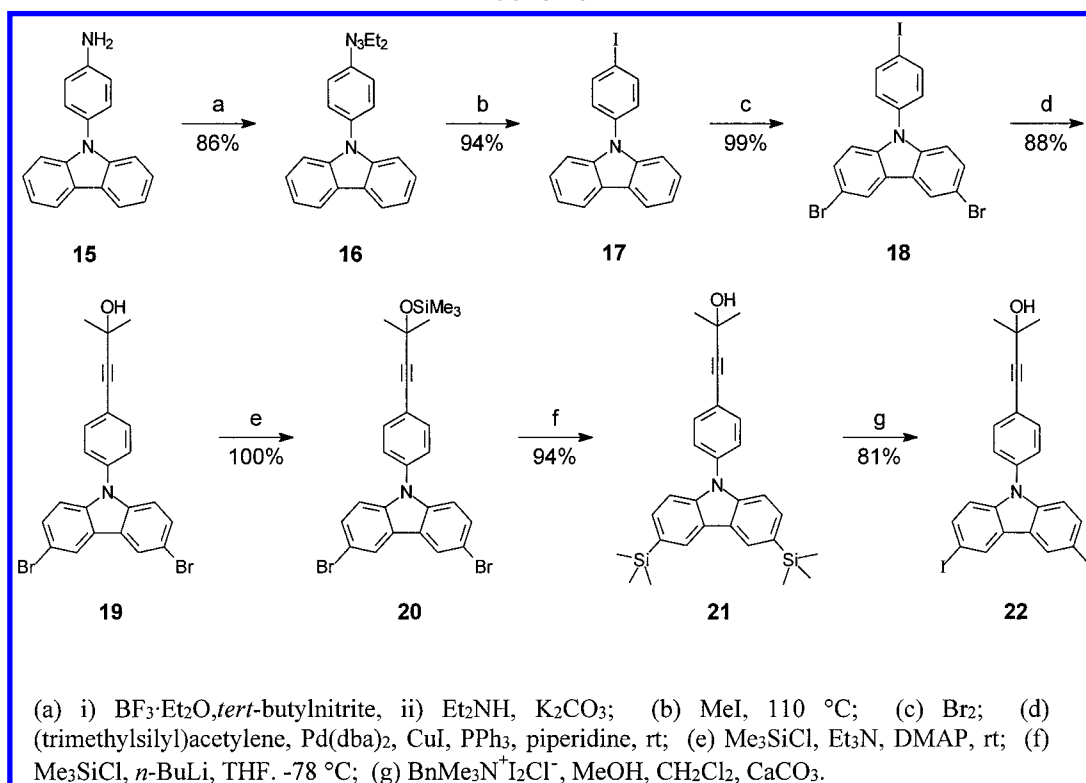| Transformations		Yields
(*t*-Bu)$_4$-(PC)$_3$-N$_3$Et$_2$ (**11**) ⟶ (*t*-Bu)$_4$-(PC)$_3$-I (**12**)		72%
(*t*-Bu)$_4$-(PC)$_3$-I (**12**) ⟶ (*t*-Bu)$_8$-(PC)$_7$-N$_3$Et$_2$ (**13**)		63%
(*t*-Bu)$_8$-(PC)$_7$-N$_3$Et$_2$ (**13**) ⟶ (*t*-Bu)$_8$-(PC)$_7$-I (**14**)		91%

methyl-but-1-ynyl group at the focal point and two iodo groups at the branching points. The iodo groups remain available to couple with terminal acetylene functionalized monodendrons to form higher generations of monodendrons. The 3-hydroxy-3-methyl-but-1-ynyl group at the focal point increases the polarity of the resulting monodendrons so as to facilitate separation of any self-coupled byproducts. 3-Hydroxy-3-methyl-but-1-ynyl group can be easily transformed to terminal acetylene groups,[38] as required for subsequent dendrimer growth. The use of a polar masking group for terminal acetylenes in the synthesis of monodisperse oligo(*p*-phenylene ethynylene)s has previously been reported.[39]
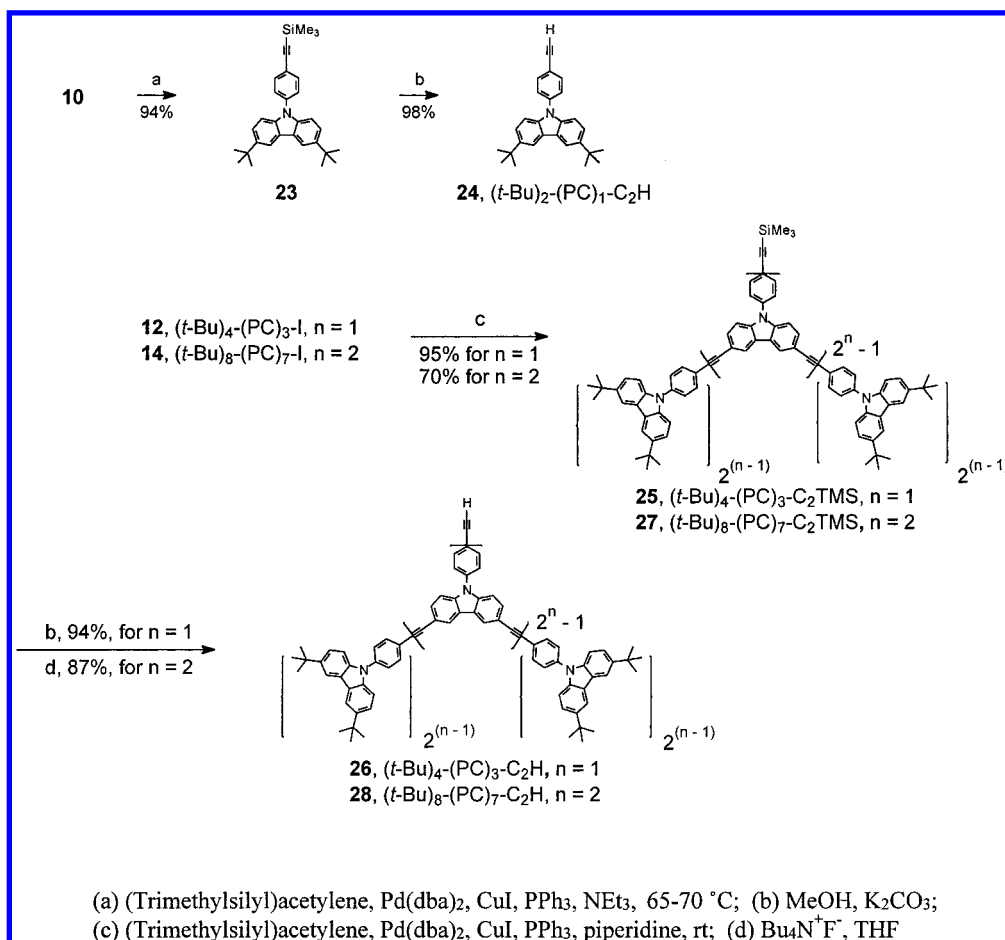
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Scheme 4

(a) i) BF$_3$·Et$_2$O,*tert*-butylnitrite, ii) Et$_2$NH, K$_2$CO$_3$; (b) MeI, 110 °C; (c) Br$_2$; (d) (trimethylsilyl)acetylene, Pd(dba)$_2$, CuI, PPh$_3$, piperidine, rt; (e) Me$_3$SiCl, Et$_3$N, DMAP, rt; (f) Me$_3$SiCl, *n*-BuLi, THF. -78 °C; (g) BnMe$_3$N$^+$I$_2$Cl$^-$, MeOH, CH$_2$Cl$_2$, CaCO$_3$.

Scheme 5

(a) (Trimethylsilyl)acetylene, Pd(dba)$_2$, CuI, PPh$_3$, NEt$_3$, 65-70 °C; (b) MeOH, K$_2$CO$_3$; (c) (Trimethylsilyl)acetylene, Pd(dba)$_2$, CuI, PPh$_3$, piperidine, rt; (d) Bu$_4$N$^+$F$^-$, THF
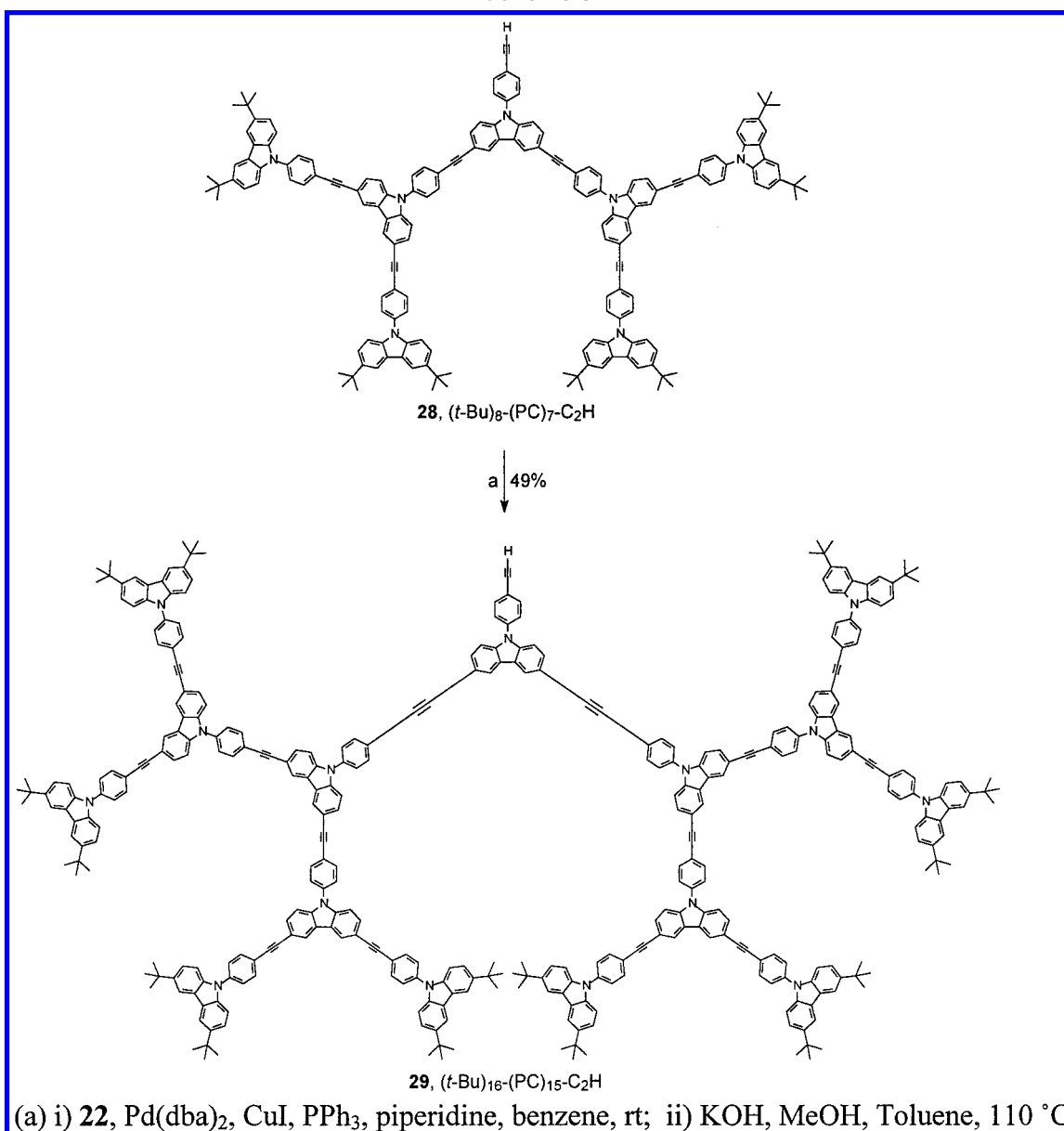
9-(4-Aminophenyl)-carbazole (**15**) was synthesized by the reduction of 9-(4-nitrophenyl)-carbazole (**1**) with stannous chloride. Compound **15** was then converted to its diazonium salt and treated with diethylamine to give triazene **16** with Doyle's method[40] and subsequently transformed to iodide **17** by heating to 110 °C in a sealed

Scheme 6

28, (*t*-Bu)$_8$-(PC)$_7$-C$_2$H

a | 49%

29, (*t*-Bu)$_{16}$-(PC)$_{15}$-C$_2$H

(a) i) **22**, Pd(dba)$_2$, CuI, PPh$_3$, piperidine, benzene, rt; ii) KOH, MeOH, Toluene, 110 °C

tube with methyl iodide. Treatment of **17** with 2 equiv of bromine gave 3,6-dibromo-9-(4-iodopheral)-carbazole (**18**). Sonogashira coupling of **18** with 1 equiv of 2-methyl-3-butyn-2-ol afforded **19**. Protection of the hydroxyl group of **19** with trimethylsilyl chloride gave **20**. Treatment of a mixture of **20** and trimethylsilyl chloride in THF with *n*-butyllithium followed by a workup with saturated ammonium chloride aqueous solution gave compound **21**. Treatment of **21** with benzyltrimethylammonium dichloroiodate in a mixed solvent of methanol and dichloromethane afforded the desired monomer **22**. Although direct conversion[41] of **20** to **22** is also possible, a large excess of *n*-butyllithium or even *tert*-butyllithium is required to generate the carbazole dianion. Using our approach, monomer **22** was realized more easily and in higher purity.

Terminal acetylene functionalized peripheral monomer (**23**) and the first two generations of monodendrons were obtained by coupling the corresponding iodides with trimethylsilylacetylene and subsequent removal of trimethylsilyl groups. Modified Sonogashira coupling with piperidine as solvent[42] was used to prepare **25** and **27**

(Scheme 5). Terminal acetylene functionalized compounds **24**, **26**, and **28** can be coupled with aryl halides to give other functionalized monodendrons or coupled with monomer **22** to give higher generation monodendrons.

The reaction of the 7-mer monodendron **28** with monomer **22** gave the 15-mer 3-hydroxy-3-methyl-but-1-ynyl monodendron (Scheme 6). Benzene was used as a cosolvent in the coupling reaction to increase the solubility of the starting materials and products. Because of significant self-coupling side reactions, an excess of **28** (2.5 equiv) was used. The 15-mer 3-hydroxy-3-methyl-but-1-ynyl monodendron was not readily soluble in common organic solvents, but interestingly, it was found to be quite soluble in carbon disulfide, a solvent with very high polarizability.[43] Self-coupling byproduct of **28** was removed by flash chromatography using a mixed sol-

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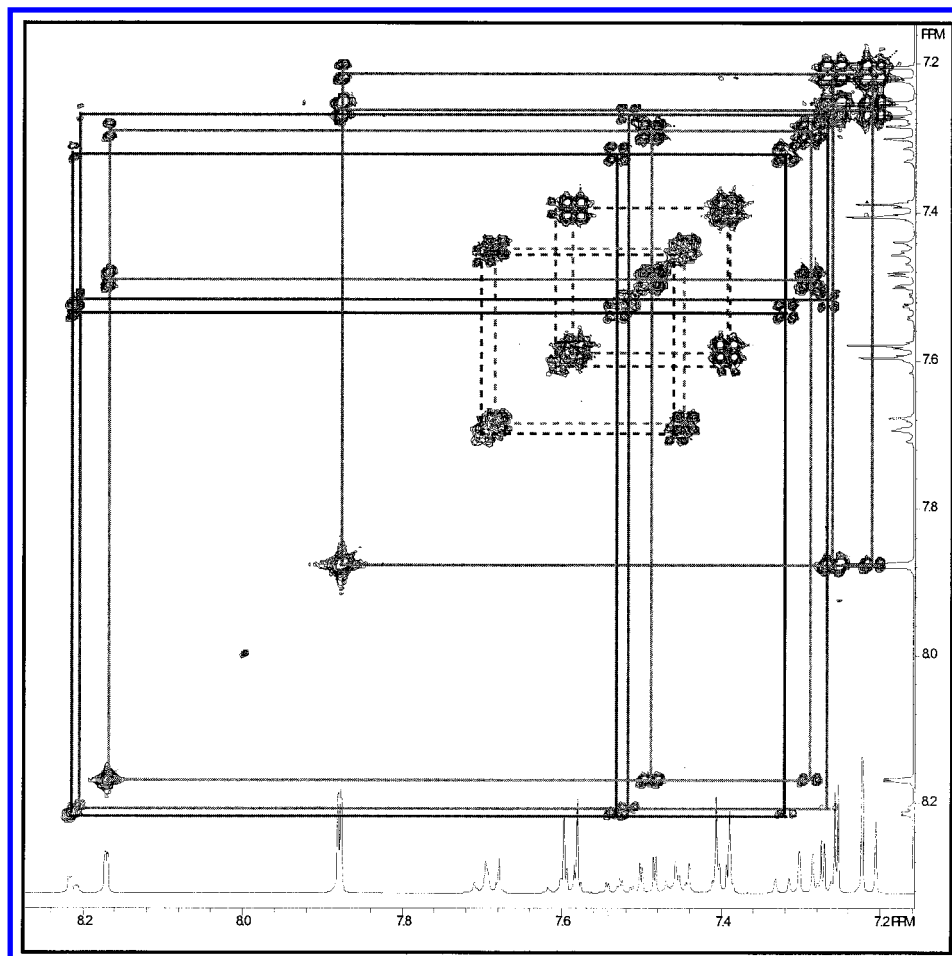
Figure 2. Aromatic region of ^{1}H COSY NMR spectrum of **29** in a mixed solvent of CS_2 and C_6D_6 with correlation map. Spectrum was recorded at a proton spectrometer frequency of 500 MHz at room temperature. The CS_2 to C_6D_6 ratio was approximately 10:1.
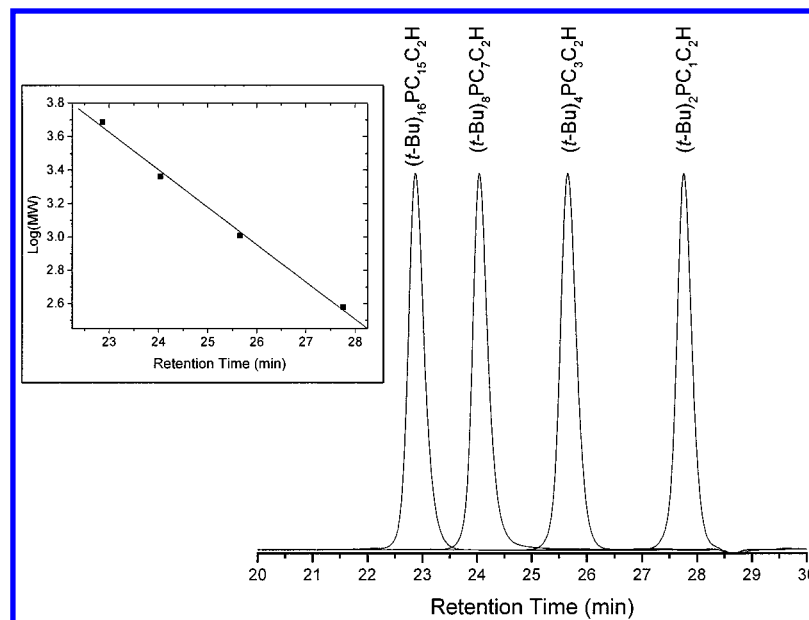
Figure 3. Normalized GPC chromatograms of 9-phenylcarbazole monomer and monodendrons bearing terminal acetylene focal points. The inset shows the linear correlation between the log of theoretical molecular weights and retention time [log(MW) = $-0.22 \cdot t + 8.78$, $R = 0.998$].

vent of carbon disulfide and benzene. It was found that better separation could be obtained when silica gel with a large pore size (150 Å) was used as the stationary phase. The resulting 3-hydroxy-3-methyl-but-1-ynyl functionalized 15-mer monodendron was then heated with

KOH in a mixed solvent of methanol and toluene at 110 °C for 1.5 h. The desired terminal acetylene functionalized 15-mer monodendron **29** was then purified by flash chromatography with carbon disulfide and benzene as the eluting solvent and 150-Å-pore silica gel as the

Table 1. Absorption Maxima, Extinction Coefficients, Fluorescence Maxima, and Fluorescence Quantum Yields of Peripheral Monomer and Monodendrons with Terminal Acetylene Focal Points[a]

| compound	λ_{max}(abs) (nm)	ϵ ($M^{-1}\,cm^{-1}$)	λ_{max}(fl)[b] (nm)	ϕ_{fl}[c]
24	320.5	1.41×10^4	379	0.09
	295.0	7.59×10^4		
	259.0	1.67×10^5		
26	346.0	9.68×10^4	381	0.60
	298.0	7.42×10^4		
	248.0	9.95×10^4		
28	347.0	2.18×10^5	381	0.63
	298.0	1.42×10^5		
29	349.5	4.36×10^5	381	0.59
	298.0	2.73×10^5		

[a] All spectra were recorded in chloroform at room temperature. [b] The excitation wavelength for fluorescence spectra was 350 nm, and the optical density was 0.100 at that wavelength. [c] The fluorescence quantum yields were determined against quinine sulfate solution in 0.1 N H_2SO_4 ($\phi_{fl} = 0.55$) as the standard.

stationary phase. Figure 2 shows the aromatic region of the ^1H COSY NMR spectrum of **29** in a mixed solvent of CS_2 and C_6D_6. The correlation map is also shown. The four different resonance signals corresponding to protons at the 4- and 5-positions of each unique carbazole are well dispersed. It is interesting to note that all eight spin systems can be identified with the help of the correlation map.

The purity of all monomers and monodendrons was verified by a combination of HPLC and gel permeation chromatography (GPC). Normalized GPC chromatograms of terminal acetylene functionalized peripheral monomer and monodendrons are shown in Figure 3. The polydispersities of all monodendrons are lower than 1.02 based on GPC data. A linear fit with good correlation was obtained when the log of the theoretical molecular weight is plotted against retention time (inset in Figure 3). The molecular weights were verified by MALDI mass spectrometry.

Spectroscopic Characterization. Electronic absorption spectra of the terminal acetylene functionalized peripheral monomer (**24**) and corresponding monodendrons were recorded in chloroform. The absorption maxima (λ_{max}) and molar extinction coefficients (ϵ) are listed in Table 1. From **24** to **26**, there is a significant red shift in the absorption maxima due to π delocalization. However, this red-shift becomes less significant with increasing generations (i.e., from **26** to **28** to **29**), suggesting that the extent of delocalization is rather limited. This limitation is possibly caused by the loss of coplanarity of the aromatic systems due steric interactions that increase with increasing dendrimer generation. All monodendrons have characteristic absorption maxima at wavelengths around 347 nm. The molar extinction coefficient increases rapidly with increasing generation as expected based on the number of 9-phenylcarbazole units per monodendron molecule.

Figure 4 shows the fluorescence spectra of the ethynyl-functionalized monodendrons in chloroform. The excitation spectra (inset in Figure 4) match the corresponding absorption spectra very well, indicating no significant chromophore impurities. Fluorescence maxima and quantum yields are listed in Table 1. The fluorescent efficiency
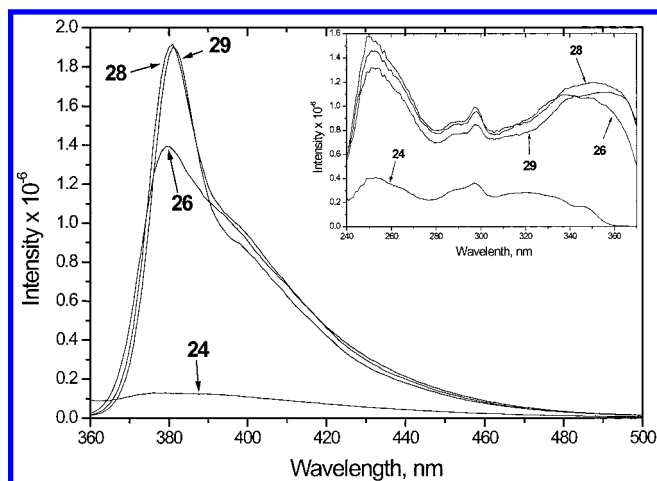
Figure 4. Fluorescence spectra of the monodendrons with terminal acetylene focal points in chloroform at room temperature. The excitation wavelength was 350 nm, and the optical density at this wavelength was 0.100. The inset shows the excitation spectra monitored at 388 nm recorded in the same solvent.

increases rapidly from monomer, to trimer, and up to 7-mer monodendron, where it appears to reach a limit. The fluorescence efficiency of the 15-mer monodendron is lower than that of the 7-mer monodendron. This is possibly because the through-space interactions between the 9-phenylcarbazole units become more significant with increasing molecular size, providing additional fluorescence quenching pathways. Molecular models of the 15-mer shows that the 9-phenylcarbazole units near the periphery can be brought close to each other through bond rotations. Similar phenomena were noted in a phenylacetylene dendrimer series.[44]

Conclusions

The first three generations of 9-phenylcarbazole monodendrons were synthesized using Sonogashira coupling reactions. With increasing generations, the solubility of monodendrons rapidly decreased. The key to the synthesis of 15-mer monodendron was the use of a monomer bearing a 3-hydroxy-3-methyl-but-1-ynyl group at its focal point, which served to mask the terminal acetylene and facilitate purification. High generations of 9-phenylcarbazole monodendrons are more soluble in solvents with high polarizability (CS_2). Electronic absorption spectra showed that there is limited delocalization between 9-phenylcarbazole units with increasing generation number. Molecular models indicate possible increased through-space interactions between 9-phenylcarbazole units in the higher generation monodendrons, consistent with results from fluorescence data.

Supporting Information Available: Experimental procedure for the preparation of all monomers and monodendrons and their characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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