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Synthesis and Characterization of 9-Phenylcarbazole Monodendrons: An Exploration of Peripheral Groups To Facilitate Purification

Zhengguo Zhu and Jeffrey S. Moore*

Roger Adams Laboratory, Departments of Chemistry and Materials Science & Engineering, and the Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana−Champaign, Urbana, Illinois 61801

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ABSTRACT: 9-Phenylcarbazole ethynylene monodendrons with 1,1,3,3-tetramethylbutyl and 3,5-di-*tert*-butyl-4-(2-methoxyethoxy)phenylene groups were synthesized. Both peripheral groups increased the solubility of the monodendrons. Only three generations of monodendrons with 1,1,3,3-tetramethylbutyl peripheral groups were realized due to difficulties in the purification of monodendron 31-mer. A peripheral monomer with two 3,5-di-*tert*-butyl-4-(2-methoxyethoxy)phenylene groups at the 3- and 6-positions of carbazole increases the solubility as well as the polarity of the monodendrons so as to facilitate the separation by adsorption chromatography, thereby enabling monodendrons up to generation four (MW = 16.6 kDa) to be realized. A monomer bearing a 3-hydroxy-3-methyl-but-1-ynyl group at its focal point as a masking group for terminal acetylene functionality was used to facilitate the removal of diacetylene byproducts.

Introduction

Materials based on spatially defined chromophore arrays are of current interest from both fundamental and technological vantage points. Of fundamental significance, these materials have proven useful for testing theoretical description of elemental steps of photosynthesis (i.e., light absorption, energy transfer, photoinduced charge generation, and charge transfer).[1,2] On the other hand, these materials hold promise as active components of thin-film transistors,[3−5] photovoltaic cells,[6] electroluminescent materials,[7,8] and photorefractive materials.[9,10] Several chromophore arrays have employed synthetic porphyrins as light-absorbing and energy-transfer component.[11−19] Well-defined arrays containing porphyrin can closely mimic natural photosynthesis systems in terms of absorption wavelength or excitation energy level.[20] However, the availability of large quantities of these materials is limited by the difficulty in the synthesis of highly functionalized soluble multiporphyrins. Large quantities of electro- and photoactive materials can be possibly prepared from readily available chromophores.

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.[21−23] Chemically, carbazole can be easily functionalized at its 3-, 6-, or 9-positions and covalently linked to other molecular moieties.[24] Due to its special photo, electrical, and chemical properties, carbazole has been used as functional building blocks in the fabrication of organic photoconductors, NLO materials, and photorefractive materials.[25−27] 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.[28−30] We recently reported the preparation of a series of well-defined dendrimers based on 9-phenylcarbazole as the fundamental building block.[31] In the syntheses of well-defined dendrimers containing a large number of chromophores within a single molecule, two problems are frequently encountered: solubility and purification. Purification problems are frequently caused by poor solubility, similarities in physical properties of the desired products, and impurities. These problems greatly hampered our initial efforts, limiting the synthesis to third-generation monodendron. It is becoming increasingly clear that the physical properties of dendrimers can be manipulated by modifying their large numbers of peripheral groups. We report here an exploration of peripheral groups to increase solubility and facilitate purification of these carbazole dendritic systems.

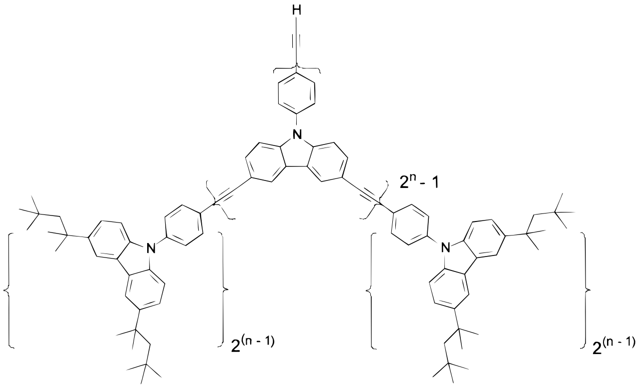

Figure 1. Structures of 9-phenylcarbazole monodenrons with 1,1,3,3-tetramethylbutyl groups at the periphery.

Results and Discussion

Previously we reported the synthesis of 9-phenylcarbazole monodendrons with *tert*-butyl groups at the periphery. It was found that the *tert*-butyl groups increase the solubility only to a limited degree, and this in turn prevented the synthesis of high generations of monodendrons. To increase the solubility of higher generations of monodendrons, monodendrons with 1,1,3,3-tetramethylbutyl groups at the 3,6-positions of peripheral carbazoles were synthesized. The structures of these monodenrons are depicted in Figure 1. Scheme 1 shows the synthesis of a 9-phenylcarbazole peripheral

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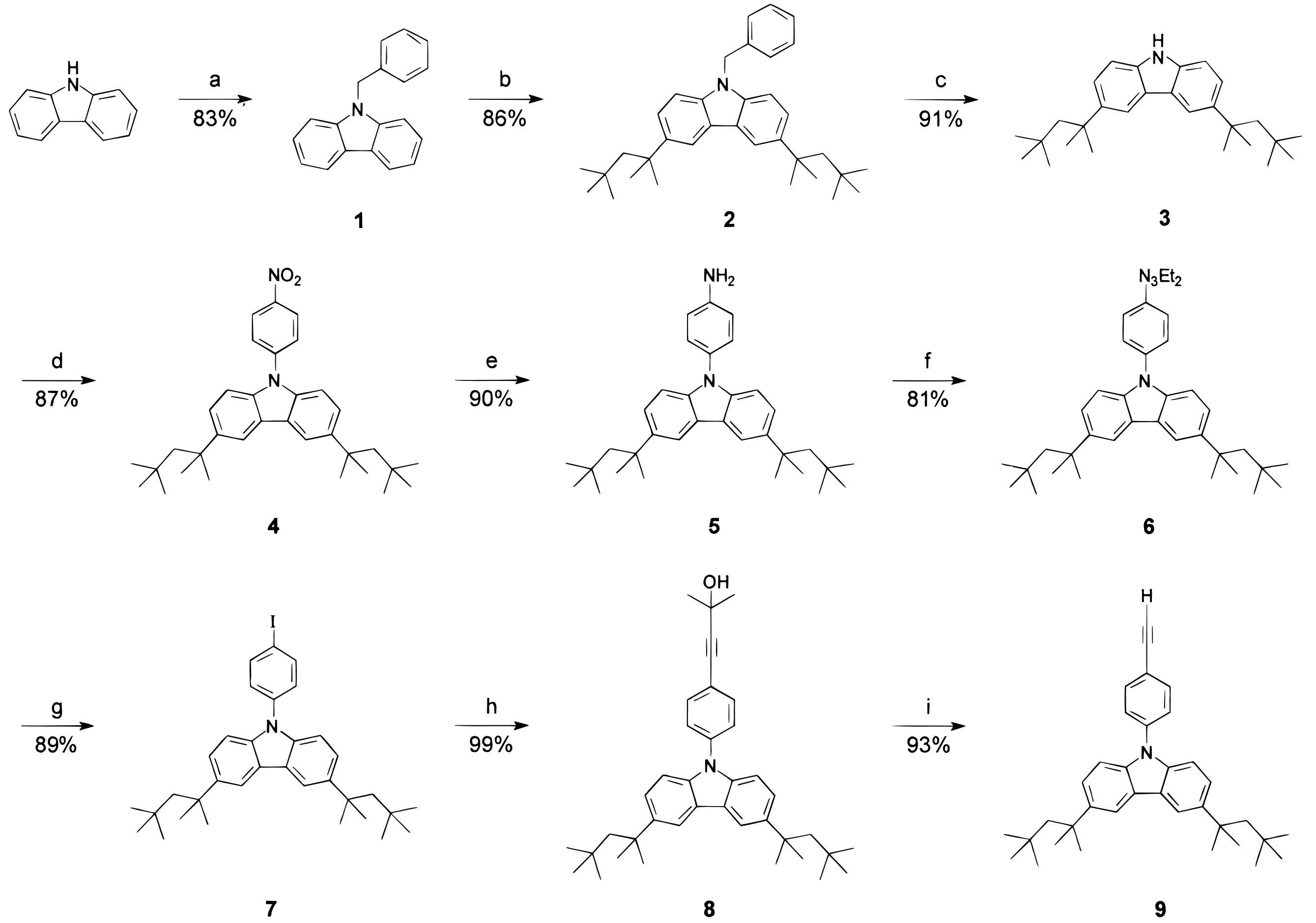
Scheme 1[a]



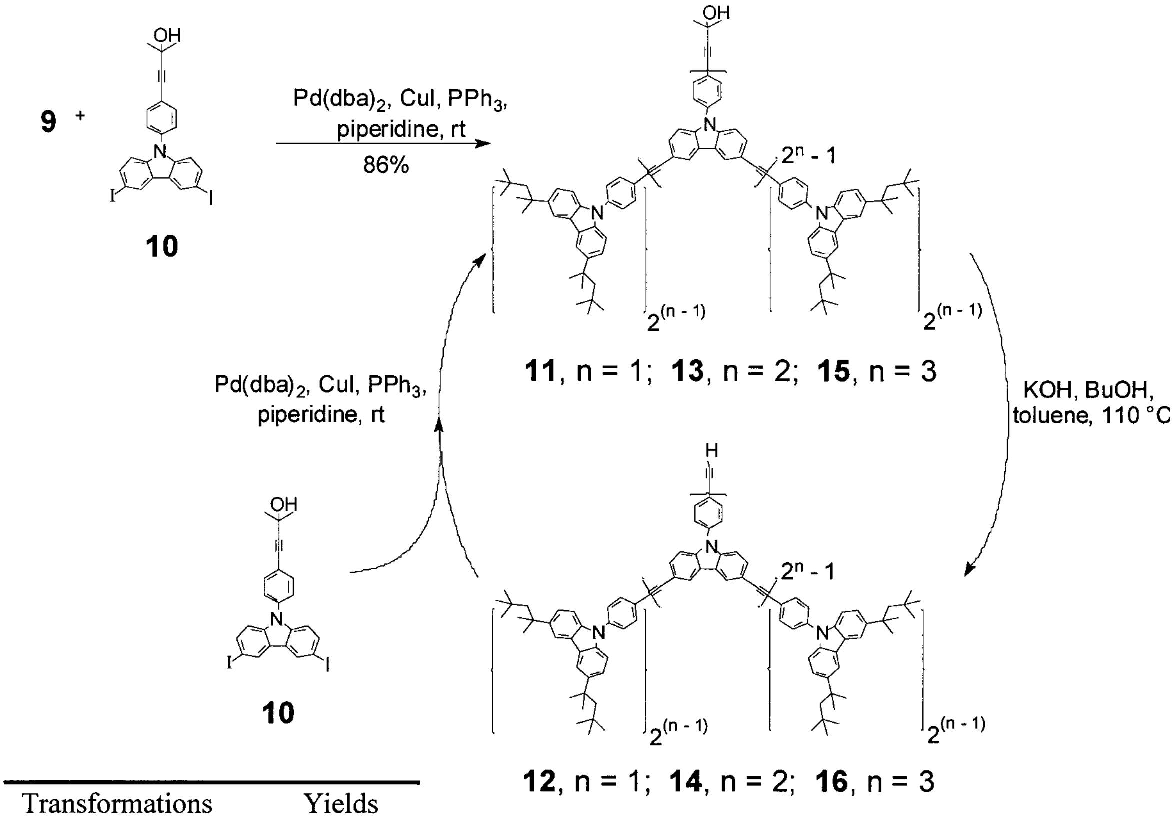
[a] (a) (i) NaH, DMF, (ii) benzyl chloride; (b) 2,4,4-trimethyl-1-pentene, $AlCl_3$, CS_2; (c) Na, NH_3; (d) (i) NaH, DMF, (ii) 4-fluoronitrobenze; (e) $SnCl_2{\cdot}2H_2O$, EtOH, 75 °C; (f) (i) $BF_3{\cdot}Et_2O$, *tert*-butyl nitrite, (ii) Et_2NH, K_2CO_3; (g) I_2, MeI, 80 °C; (h) 2-methyl-3-butyn-2-ol, $Pd(dba)_2$, CuI, PPh_3, piperidine, rt; (i) KOH, BuOH, toluene, 110 °C.

monomer with two 1,1,3,3-tetramethylbutyl groups at the 3,6-positions of carbazole. Carbazole was treated with sodium hydride in DMF followed by benzyl chloride to afford 9-benzylcarbazole (**1**). Friedel–Crafts alkylation of **1** with 2,4,4-trimethyl-1-pentene catalyzed by $AlCl_3$ gave 9-benzyl-3,6-bis(1,1,3,3-tetramethylbutyl)carbazole (**2**) in good yield. The benzyl group was then removed with sodium in liquid ammonia to afford 3,6-bis(1,1,3,3-tetramethylbutyl)carbazole (**3**). Direct Friedel–Crafts alkylation of carbazole with 2,4,4-trimethyl-1-pentene gave a significant amount of side products that were difficult to separate. Treatment of **3** with sodium hydride followed by 4-fluoronitrobenzene gave 9-(4-nitrophenyl)-3,6-bis(1,1,3,3-tetramethylbutyl)carbazole (**4**), which was reduced with stannous chloride to give 9-(4-aminophenyl)-3,6-bis(1,1,3,3-tetramethybutyl)carbazole (**5**). Compound **5** was then converted to its diazonium salt and treated with diethylamine to give triazene **6**, which was transformed to the corresponding iodide **7** by heating to 80 °C in a sealed tube with methyl iodide and iodine.[32] The coupling of **7** with 2-methyl-3-butyn-2-ol in piperidine[33] gave 9-(4-(3-hydroxy-3-methylbutynyl)phenyl)-3,6-bis(1,1,3,3-tetramethybutyl)carbazole (**8**) in good yield. Treatment of **8** with KOH in a mixed solvent of butanol and toluene at 110 °C[34] for 1.5 h afforded the terminal acetylene functionalized peripheral monomer **9**.

The synthesis of monodendrons with **9** as peripheral monomer is outlined in Scheme 2. Focal point monomer 3,6-diodo-9-(4-(3-hydroxy-3-methyl-but-1-ynyl)phenyl)-carbazole (**10**) was synthesized from carbazole in nine steps.[31] This monomer has a 3-hydroxy-3-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-methylbut-1-ynyl group at the focal point increases the polarity of the resulting monodendrons so as to facilitate separation of any self-coupled byproducts. The 3-hydroxy-3-methylbut-1-ynyl group can be easily transformed to terminal acetylene groups,[34] as required for subsequent dendrimer growth. Alternatively repeating the coupling reaction and the transformation of the 3-hydroxy-3-methylbut-1-ynyl group to a terminal acetylene group smoothly afforded 9-phenylcarbazole monodendrons up to 15-mer. Piperidine was used as solvent for all the coupling reactions so that the reactions can be conducted at room temperature.[33] It was found that 150 Å pore-size silica gel was a more effective adsorbent in flash chromatography for 15-mer monodendrons than the common 60 Å pore-size silica gel, probably because large-pore-size silica gel provides more effective surface area for large molecules.

All the monodendrons up to 15-mer can be obtained in high purity, as verified by a combination of HPLC and gel permeation chromatography (GPC). The polydispersities of all monodendrons are found to be lower than 1.02 based on polystyrene standards. It was found

Scheme 2



10

11, n = 1; **13**, n = 2; **15**, n = 3

10

12, n = 1; **14**, n = 2; **16**, n = 3

Transformations	Yields
11 → **12**	87%
12 → **13**	83%
13 → **14**	90%
14 → **15**	72%
15 → **16**	92%

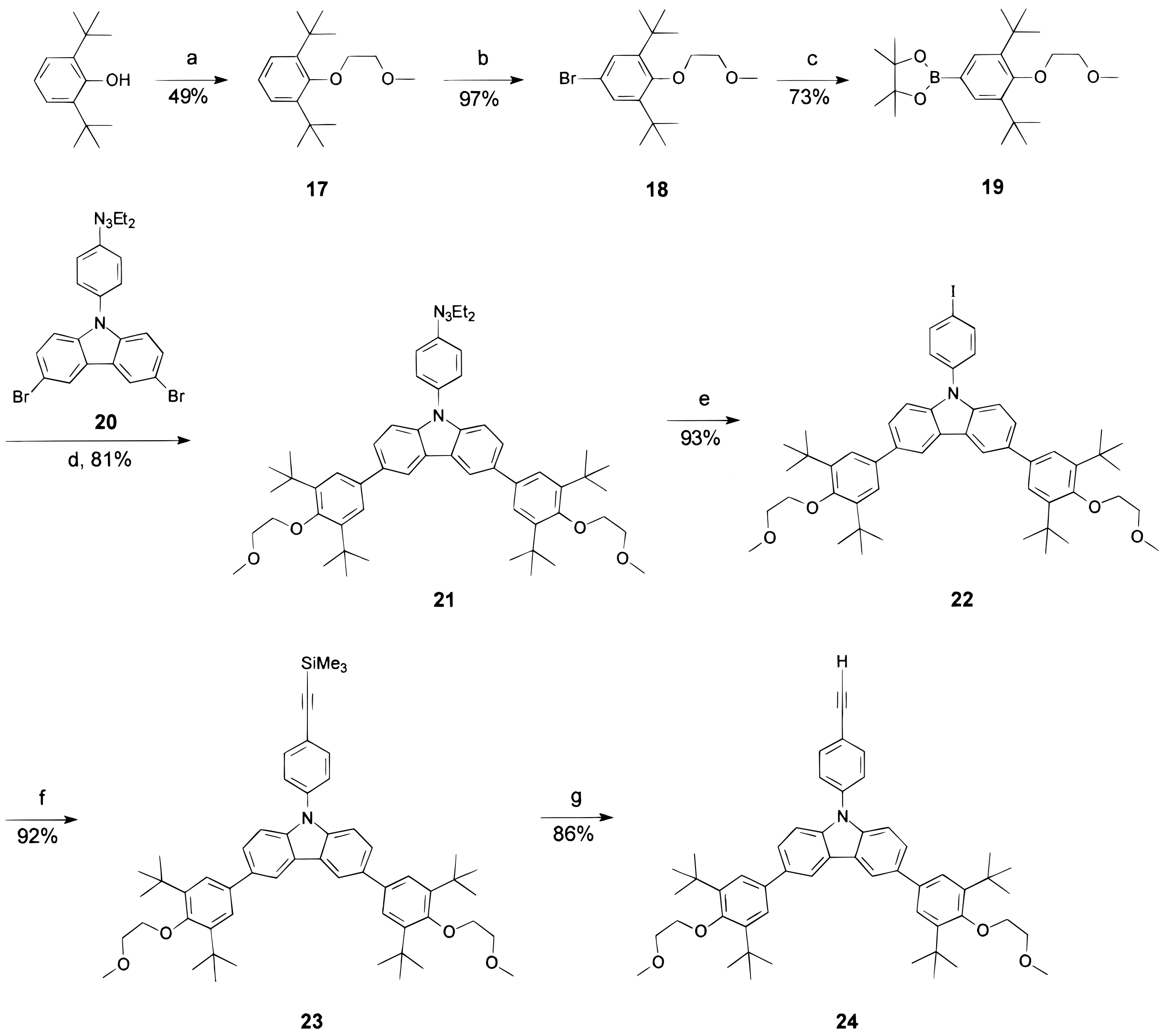
that the extended branched alkyl peripheral groups did provide monodendrons with higher solubility. All compounds in this series have higher solubility in common organic solvents than the corresponding monodendrons with *tert*-butyl groups at the peripheral. Monodendron 15-mer is readily soluble in benzene, THF, chloroform, and dichloromethane.

Attempts were made to prepare 31-mer monodendron. However, the coupling reaction of terminal acetylene functionalized monodendron **16** with monomer **10** yielded a mixture of products that was difficult to purify. HPLC of the crude reaction showed three major peaks corresponding to oxidative self-coupling dimer of 15-mer monodendron, the 31-mer monodendron, and the precursor 15-mer monodendron. The dimer resulting from self-coupling could not be resolved from the desired 31-mer monodendron by GPC. Because of similarity in the retention times of these species, the purification of 31-mer monodendron was not successful.

Adsorption chromatography using silica gel as stationary phase has proven to be very effective in the separation of small molecules. However, complication arises when large-size molecules are involved.[35] In the case of dendrimer purification, the larger number of functional groups present in higher generations of dendrimer tends to increase their adsorption on adsorbents. At the same time, the size exclusion effect, which increases with increasing dendrimer generations, tends to decrease the retention on the adsorbents. One way to get around this problem may be to attach suitable polar functional groups to the peripheral monomer, so that the polarity of the dendrimers increases rapidly due to the increasing number of polar groups in each molecule. The increased adsorption strength in higher generations of dendrimers may overcome the size exclusion effect to facilitate separations of dendrimers of different sizes by adsorption chromatography.

To increase the solubility as well as the adsorption of monodendrons on silica gel to facilitate purification, 3,5-di-*tert*-butyl-4-(2-methoxyethoxy)phenylene was used as the peripheral group. Monodendrons with these peripheral groups shown in Figure 2 were synthesized. The increasing number of polar 2-methoxyethyl ether groups with increasing generation facilitated separation of monodendrons. The synthesis of peripheral monomer bearing 3,5-di-*tert*-butyl-4-(2-methoxyethoxy)phenylene groups at 3,6-positions of carbazole is shown in Scheme 3. Commercially available 2,6-di-*tert*-butylphenol was treated with sodium hydride in DMF, and the resulting phenoxide was reacted with 2-methoxybromoethane to afford 2,4-di-*tert*-butyl-(2-methoxyethoxy)benzene (**17**). Because of the steric hindrance of the two adjacent *tert*-butyl groups, this reaction was very slow. Tetrabutylammonium iodide was used to accelerate the reaction; however, there was still a significant amount of starting material left even after heating to 110 °C for 48 h. The product could be easily separated from the starting material due to its higher polarity. Bromination of **17**

Scheme 3[a]



[a] (a) (i) NaH, (ii) 2-bromoethyl methyl ether; (b) Br_2, CH_2Cl_2; (c) (i) *n*-butyllithium, THF, (ii) 2-ethoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane; (d) $Pd(dba)_2$, $(o\text{-toly})_3P$, Na_2CO_3, 90 °C; (e) MeI, 110 °C; (f) (trimethylsilyl)acetylene, $Pd(dba)_2$, CuI, PPh_3, piperidine, rt; (g) KOH, THF, methanol, rt.

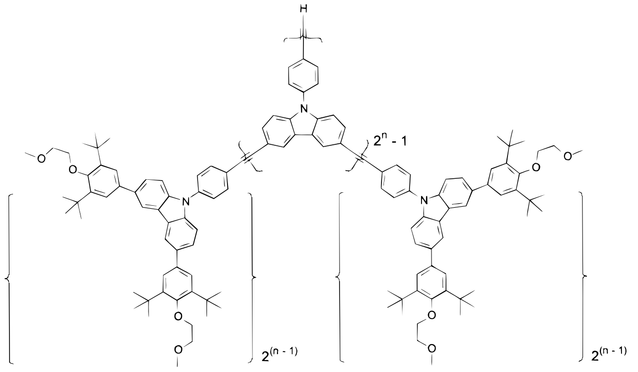


Figure 2. Structures of 9-phenylcarbazole monodenrons with 3,5-di-*tert*-butyl-4-(2-methoxyethoxy)phenylene groups at the periphery.

smoothly afforded 2,6-di-*tert*-butyl-4-bromo-(2-methoxyethoxy)benzene (**18**). To attach the 3,5-di-*tert*-butyl-4-(2-methoxyethoxy)phenylene group to carbazoles, boronic acid pinacol ester (**19**) was prepared, setting the stage for Suzuki coupling.[36] 2-Aryl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane derivatives are easier to purify than their corresponding boronic acids and have been successfully used in Suzuki coupling reactions to construct several interesting molecular architectures.[37,38] Treatment of **3** with *n*-butyllithium followed by 2-ethoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane at −78 °C in THF afforded boronic acid pinacol ester **19** in good yield. The 2-ethoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was prepared by heating triethyl borate and pinacol in toluene following the literature procedure.[39] 3,6-Dibromo-9-(4-(3,3-diethyltriazenyl)phenyl)carbazole (**20**) was prepared from carbazole in four steps.[31] Suzuki coupling of **19** with **20**, using tri-*o*-tolylphosphine as ligand and $Pd(dba)_2$ as palladium source, afforded the desired peripheral monomer precursor (**21**) with 3,3-diethyltriazene at the focal point. The reaction was complete within 3 h with good yield. Heating **21** with methyl iodide in a sealed tube under nitrogen to 110 °C[40] afforded the iodide functionalized peripheral monomer **22**. Sonogashira coupling[33,41] of **22** with trimethylsilylacetylene using piperidine as solvent gave the trimethylsilylethyne functionalized peripheral monomer **23**. Treatment of **23** with tetrabutylammonium fluoride afforded the peripheral monomer **24** with two 3,5-di-

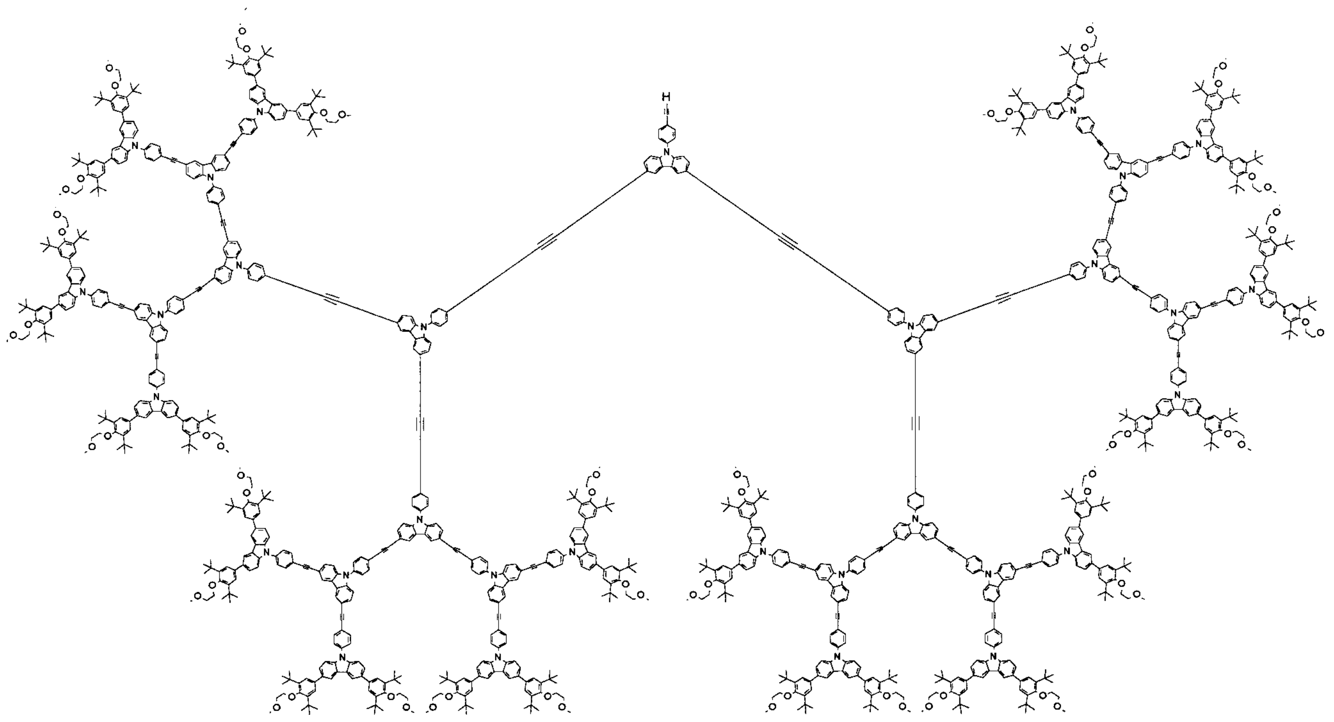


Figure 3. Structure of a monodendron containing 31 9-phenylcarbazole monomer units.

tert-butyl-4-(2-methoxyethoxy)phenylene groups at the 3,6-positions of carbazole.

The synthesis of 9-phenylcarbazole monodendrons with 3,5-di-*tert*-butyl-4-(2-methoxyethoxy)phenylene groups at the periphery is shown in Scheme 4. Peripheral monomer **24** was coupled to monomer **10** under palladium catalysis to afford trimer monodendron **25** with 3-hydroxy-3-methylbut-1-yne group at the focal point. The product was easily purified due to its appreciably higher polarity than starting materials and possible self-coupling products of terminal acetylenes. The 3-hydroxy-3-methylbut-1-yne group at the focal point of **25** was then converted to terminal acetylene by heating a solution of **25** in toluene with KOH and methanol to 110 °C. By alternatively repeating the coupling reaction of monodendrons with monomer **10** and the conversion of 3-hydroxy-3-methylbut-1-yne group to terminal acetylene, monodendrons up to 31-mer were successfully prepared. All reactions could be scaled up without much complication. All compounds were purified by flash chromatography with silica gel as adsorbents. Silica gel with 150 Å pore size was used in the purification of 15-mer and 31-mer monodendrons. High-generation monodendrons was easily separable from low-generation monodendrons because high-generation monodendrons contain more polar peripheral groups. Monodendrons with the 3-hydroxy-3-methylbut-1-yne group were all separable from self-coupling byproduct due to the presence of a polar hydroxyl group at the focal point. These monodendrons were all purified until free of self-coupling byproducts as verified by HPLC before being subjected to the next step of reaction. The full structure of a monodendron containing 31 9-phenylcarbazole units that has been realized is shown in Figure 3.The purity of all monodendrons was found to be higher than 99% by HPLC and gel permeation chromatography (GPC). Normalized GPC chromatograms of terminal acetylene functionalized peripheral monomer and monodendrons are overlaid in Figure 4. 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 versus GPC retention time (inset in Figure 4).

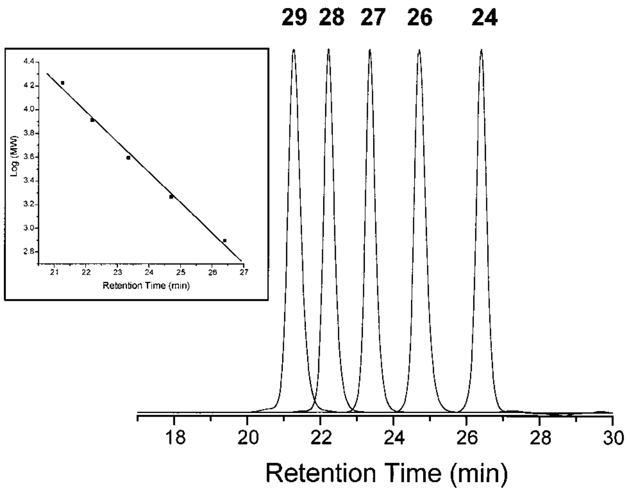
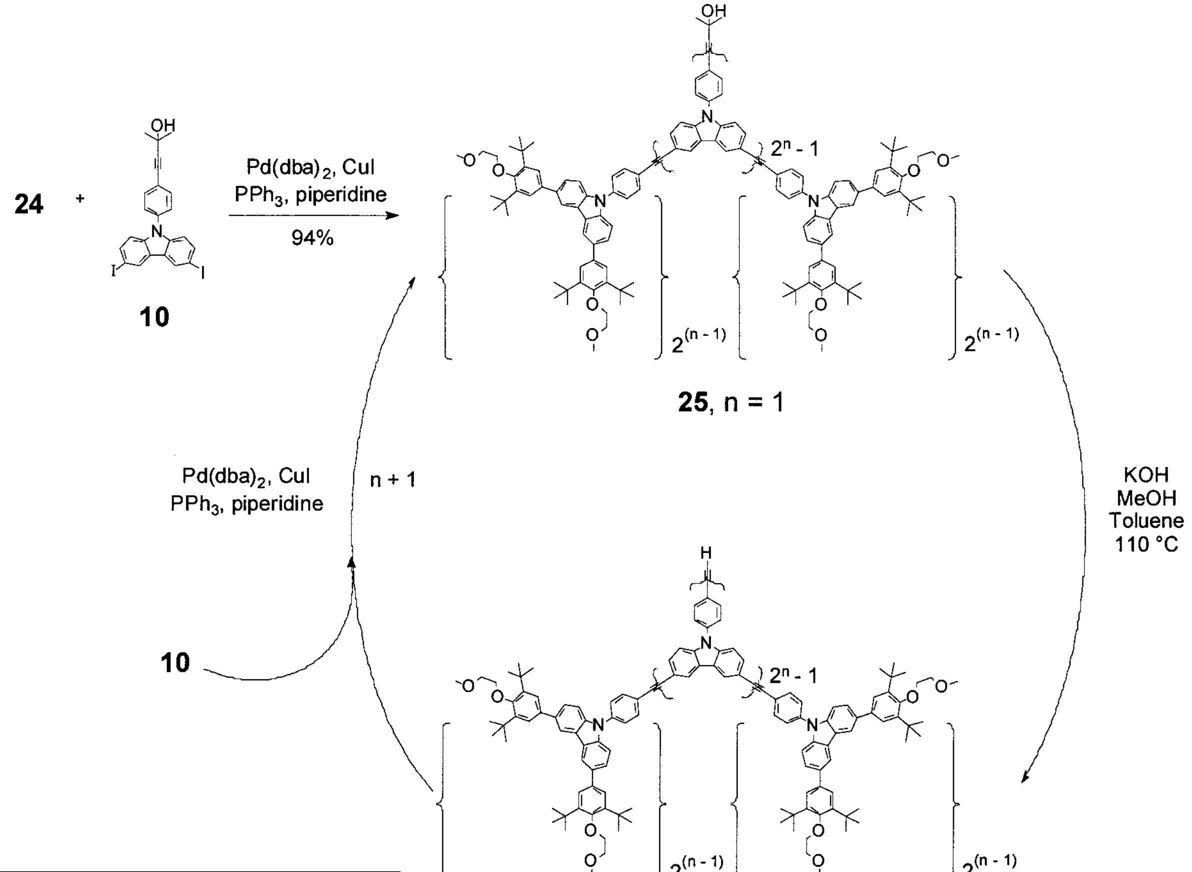


Figure 4. Normalized GPC chromatograms of terminal acetylene functionalized monomer **24** and monodendrons with 3,5-di-*tert*-butyl-4-(2-methoxyethoxy)phenylene groups at the periphery. The inset shows the linear correlation between log of theoretical molecular weights versus retention time [log(MW) = $-0.26t + 9.62$; $R = 0.997$].

The aromatic regions of ^{1}H NMR spectra of the peripheral monomer **24** and monodendrons **26**, **27**, **28**, and **29** are shown in Figure 5. In lower generations, well-dispersed and resolved signals are observed. With the increase of generation, aromatic regions of the ^{1}H NMR spectra become much more complicated. By using mixed solvent of C_6D_6 and CS_2, better dispersion of resonance signals was obtained. Signals due to the resonance of the protons at the 4,5-positions of carbazoles are well dispersed and easily assigned for most of the monodendrons.

Scheme 4



25, n = 1

26, n = 1; **27**, n = 2; **28**, n = 3; **29**, n = 4.

Transformations	Yields
25 → **26**	87%
26 → **27**	82%
27 → **28**	63%
28 → **29**	27%

All these monodendrons were also characterized by matrix-assisted laser desorption ionization mass spectroscopy (MALDI). It was found that the ionization properties of these molecules were closed related to the molecule size and choice of matrix. The molecular ion peak and peaks corresponding to the loss of *tert*-butyl groups were observed in most cases. Since the purity of the samples was carefully verified by HPLC and GPC as well as NMR and elemental analysis, the multiple ionic species is believed to be formed during the course of MALDI experiment. By using *trans*-retinoic acid as matrix, MALDI of the trimer monodendron **26** showed a molecular weight of 1847.85 (theoretical molecular weight 1846.52). A fragment peak at 1789.1 was also observed, which corresponds to the loss of one *tert*-butyl group. The MALDI of 7-mer monodendron **27** was acquired using indole-3-acrylic acid as matrix, and a molecular ion with mass 3957.64 (theoretical molecular weight 3955.35) was observed along with fragments due to loss of *tert*-butyl groups. The MALDI of 15-mer **28** monodendron was acquired using *trans*-retinoic acid as matrix, and a molecular ion with mass of 8189.2 (theoretical molecular weight 8180.0) was observed along with fragments due to loss of *tert*-butyl groups. MALDI of 31-mer monodendron **29** required *trans*-retinoic acid as matrix, providing a molecular ion with mass of 16 633.2 (theoretical molecular weight 16 623) along with fragments due to loss of *tert*-butyl groups

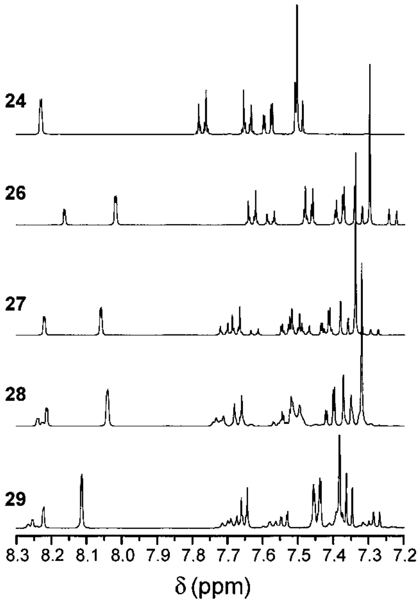


Figure 5. Stacked plot of aromatic regions of ^{1}H NMR spectra of peripheral monomer **24** (400 MHz, 3:2, CS$_2$:CD$_2$Cl$_2$) and monodendrons **26** (400 MHz, 10:1, CS$_2$:C$_6$D$_6$), **27** (400 MHz, 10:1, CS$_2$:C$_6$D$_6$), **28** (400 MHz, 10:1, CS$_2$:C$_6$D$_6$), and **29** (500 MHz, 5:1, CS$_2$:C$_6$D$_6$) with terminal acetylene at the focal point.

with mass of 16 575.7 and 16 518.1. All compounds in this series are appreciably soluble in common organic solvents such as benzene, THF, chloroform, and dichloromethane.

Conclusions

The solubility of the monodendrons was significantly increased with 1,1,3,3-tetramethylbutyl peripheral groups at the periphery 9-phenylcarbazole monodendrons. However, only three generations of monodendrons with this peripheral group were realized due to difficulties in the purification of mondendron 31-mer. This same problem was encountered in our earlier synthesis. A peripheral monomer with two 3,5-di-*tert*-butyl-4-(2-methoxyethoxy)phenylene groups at the 3,6-positions of carbazole increases the solubility as well as the polarity of the monodendrons so as to facilitate the separation by adsorption chromatography. A monomer bearing a 3-hydroxy-3-methylbut-1-ynyl group at its focal point as a masking group for terminal acetylene functionality facilitated the removal of diacetylene byproducts. Monodendrons up to generation four (MW = 16.6 kDa) were realized. The photophysical characterization of the multiple-chromophore arrays will be reported in due course.

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Supporting Information Available: Synthetic procedures, GPC traces, and ^{1}H NMR spectra of terminal acetylene functionalized monodendrons. This material is available free of charge via the Internet at http://pubs.acs.org.

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