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Dendritic Structure Having a Potential Gradient: New Synthesis and Properties of Carbazole Dendrimers

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Abstract: A new synthetic route for carbazole dendrimers was discovered using the copper-catalyzed N-arylation reaction. This synthetic route allowed synthesizing the fourth generation carbazole dendrimer and several derivatives for the first time. The crystal structure, Mark−Houwink−Sakurada plots, and UV−vis and fluorescence studies showed that the dendritic carbazole backbone has a rigid and highly twisted structure. From the measurement of the redox potential of the ferrocene derivatives, the IR spectra of the benzophenone derivatives, and complexation behavior of the phenylazomethine derivatives, the inductive electron-withdrawing effect of the carbazole dendron was revealed. This suggested that the summation of this electron withdrawal from each layer may produce a potential gradient such that the outer layer is electron-rich and the inner layer is electron-poor in the carbazole dendron. By assignment of the ^{1}H and ^{13}C NMR spectra of the dendron, the existence of this kind of potential gradient was proved. Overall, these data show the π-polarization substituent effect of the carbazole unit, and their summation determines the potential gradient in the repeating dendritic structure of the carbazole dendrimer.

Introduction

Controlling the energy level (structure) of molecules (molecular systems) is one of the most important factors that controls the behavior of electrons (molecules). For example, it is well known that all natural proteins have finely controlled potential (electrical and mechanical) structures and that the photosynthesis system has a precisely tuned step-type potential structure that provides an efficient charge separation, charge transfer, and reduction.[1] The importance of the energy level (structure) is also generally known in the area of electronics. The step-type potential structure for the charge transfer and barrier-type potential structure to block the charge is constructed by laminating several molecules for efficient organic light emitting diodes,[2] and in the inorganic field, the square well potential is used for laser diodes.[3] As just described, the geometric potential structures show impressive functions, and the construction and manipulation technique of the potential structures (not only the HOMO−LUMO level) should be essential in several fields of chemistry.

Theoretically, laminating or binding several molecules having several energy levels is the easiest approach to construct small to large scale geometric potential structures. Actually, the construction of one-dimensional step-type potentials[4] and a repeated donor−acceptor structure[5](analogy of square well potential) is not very difficult. However, to construct more complicated (higher dimension) potential structures, the difficulty in the synthesis, the unstable conformation, the contribution and interaction of the molecules, and the unevenness of the molecules (mainly in polymer systems) becomes a crucial problem. Therefore, a new approach to alleviate these problems is required in order to allow the full control of the potential structure.

Dendrimers[6] are perfectly branched polymers and have been the focus of constant attention for the past two decades. Their unique molecular structure and functions are not only used for fundamental research but also applied to catalysis,[7] drug delivery,[8] and electronic materials.[9] One of the significant characteristics of the dendritic materials is the stable conformation, i.e., the clear distinction of the inner (core) and outer

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(periphery) units. However, in high-generation soft-type dendrimers (PAMAM,[6d] poly benzyl ether type,[10] etc.) the back-folding effect and significant vibration of the dendrimer are present.[6b,11] Therefore, it is difficult to say that each layer of the dendrimer is equivalent. On the other hand, the conformation of rigid-type dendrimers (poly phenylene,[12] etc.) are considered to be relatively stable. As previously mentioned, this stable and rigid conformation satisfies the demand for constructing a geometric potential structure in the molecule. Therefore, rigid dendrimers can possibly have an intramolecular spherical potential structure, and an excellent and exclusive example of this is the phenylazomethine dendrimer.[13] The phenylazomethine dendrimer is one of the rigid-type dendrimers, and it has been reported that this dendrimer has unique "stepwise radial complexation" ability.[13a] This phenomenon is expressed by the difference in the basicity of each layer.[14] In other words, the difference in the electronic density of each layer, i.e., the phenylazomethine dendrimer has an inner layer electron-rich and outer layer electron-poor type spherical potential structure. The mechanism of the expression of this potential gradient is still unclear, but some factors have been clarified. One is the electron donation of the outer-layer azomethine to the inner layer,[14] and another is the rigid dendrimer structure.[15] Therefore, by choosing a dendritic structure that satisfies these requirements, it is expected that the dendrimer can express a potential gradient in the repeating dendritic backbone.

Carbazole is a common heterocyclic compound with interesting photo- and electro-chemistries,[16] and it is known as an OPC (organic photo conductor)[17] or a hole-transporting material.[18] Naturally, several trials to use this compound as the outer layer of the dendrimer[19] and as the dendritic backbone were done,[20−22] and interesting functions were observed. We focused on the rigid carbazole backbone and expected that this dendrimer conforms to the previously mentioned assumption to express the potential gradient in the dendritic backbone. However, the crucial problem of this dendrimer was its difficult synthesis due to the side reactions of the Ullmann reaction-based synthesis.[21a] Due to this problem, there has been no report of a fourth generation dendron, and the statistical and basic study of the carbazole dendron has been rarely reported. Therefore, in this paper, we first report the new copper-catalyzed N-arylation reaction-based[23] synthesis of the fourth generation dendron. We also

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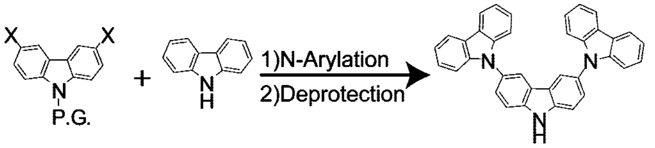
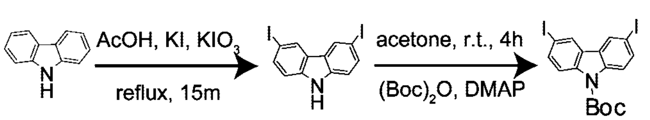
Scheme 1. Basic Strategy for Preparation of the Carbazole Dendrons



Scheme 2. Synthesis of Boc-Protected 3,6-Diiodocarbazole



I$_2$BocCz

report the basic property of the carbazole dendrons along with several measurements of the carbazole dendron substituted compounds. Finally, with the complete analysis of the NMR spectra, we reveal the intramolecular potential gradient of the carbazole dendrimer.

Results and Discussion

1. Synthesis of Carbazole Dendrimers. The basic strategy for the preparation of the carbazole dendron is outlined in Scheme 1. In recent reports,[20−22] the classical Ullmann reaction[24] was used as the N-arylation reaction, and acetyl[20a] or tosyl[20c] groups were used for the protecting group. However, the side reactions that were caused by the oxidative conditions and the high temperature (over 165 °C) of the Ullmann reaction was a significant problem[21a] of this synthetic route. Due to this, synthesizing high generation dendrons is very difficult, and there is no report of the G4 dendron. Therefore, as a new N-arylation reaction, we focused on the reaction that occurs under relatively mild conditions (110 °C) as reported by Buchwald et al.[23] For applying this reaction, the *tert*-butoxycarbonyl (Boc) group was chosen as protecting group.

The carbazole dendrons were synthesized as described in Schemes 2 and 3. First, 9-Boc-3,6-diiodocarbazole (**I$_2$BocCz**) was synthesized by the iodination of the carbazole[20a] followed by Boc protection of the amine group (Scheme 2).[25] Next, **I$_2$BocCz** and the carbazole were reacted by the N-arylation reaction,[23] and then the mixture was deprotected with a mixture of toluene, trifluoroacetic acid (TFA), water, and anisole (72 h). From the mixture, the carbazole G2 dendron (**CzG2on**) was isolated in 58% yield (two steps). The deprotection reaction with TFA worked much faster in chloroform without additive reagents (4 h), though, under this condition, slight accretion of the *t*-butyl cation was observed.[26] This kind of addition reaction of the *t*-butyl cation to the indole ring (tryptophan) is reported in the solid-phase peptide synthesis. Usually to inhibit this side reaction, the thiol, phenol, water, anisole, etc. are added to the reaction mixture as an electrophile scavenger.[26] Therefore, water and anisole were added to the reaction to suppress the addition reaction. Hence, the reaction speed decreased, and the side reaction became negligible. The carbazole G3 (**CzG3on**) and G4 dendrons (**CzG4on**) were synthesized by repeating this N-arylation and deprotection reactions in 75% and 47% yields (two steps), respectively (Scheme 3).

To measure the basic properties of the carbazole dendrons, the phenyl, benzophenone, phenylazomethine, and ferrocene substituted carbazole dendrons were synthesized (Scheme 4). The phenyl (**G*n*Ph**), benzophenone (**G*n*B**), and ferrocene (**G*n*Fc**) derivatives were synthesized by the copper-catalyzed N-arylation reaction between the iodinated compounds[27,28] and carbazole dendrons. The phenylazomethine derivatives (**G*n*A**) were synthesized by a dehydration reaction using TiCl$_4$[13b] between the aniline and benzophenone substituted carbazole dendrons (Scheme 4). All products were identified by ^{1}H NMR, ^{13}C NMR, MALDI-TOF MS, elemental analysis, and HPLC analysis (see Supporting Information).

2. Structure of Carbazole Dendrons. The intrinsic viscosity and hydrodynamic radius of the carbazole dendrons (compounds with MW over 450) were measured and their Mark−Houwink−Sakurada plots[6b,29] and generation−hydrodynamic radius plots were drawn (Figures 1, and S6). In the Markhouwink−Sakurada plot, all the carbazole dendrons gave a linear curve and the slopes of the lines were in the range of 0.2−0.5.[29] Similarly, the generation−hydrodynamic radius plot gave a linear curve. These results suggest that the carbazole dendron has a completely branched structure without back-folding due to the rigid carbazole backbone.

Single crystals of **G1B**, **G2B**, **G1Fc**, and **G2Fc** have been prepared, and X-ray single crystal structural analysis has been completed (Figures S29−31, and 2). In the crystal structures of **G2B**, **G1Fc**, and **G2Fc**, the dihedral angles of benzene−carbazole and carbazole−carbazole were in the range of 50−70°. On the other hand, in the crystal of **G1B**, it was around 40° due to the donor (carbazole) acceptor (benzophenone) interaction[20d,30] (the UV−vis absorption spectra of G1B in several solvents are suggesting this; see Figure S7 in the Supporting Information). These crystal structures suggest that carbazole dendrons usually have a twisted structure, and the dihedral angle increases when the generation of carbazole dendron increases due to steric hindrance. This result matches also the 3D model of **G*n*Ph** optimized by the Gaussian 03 (DFT calculation with STO-3G as the base function, see Supporting Information).[31]

The UV−vis absorption and fluorescence spectra of **G*n*Ph** were measured (Figure 3). The absorption edge was red-shifted

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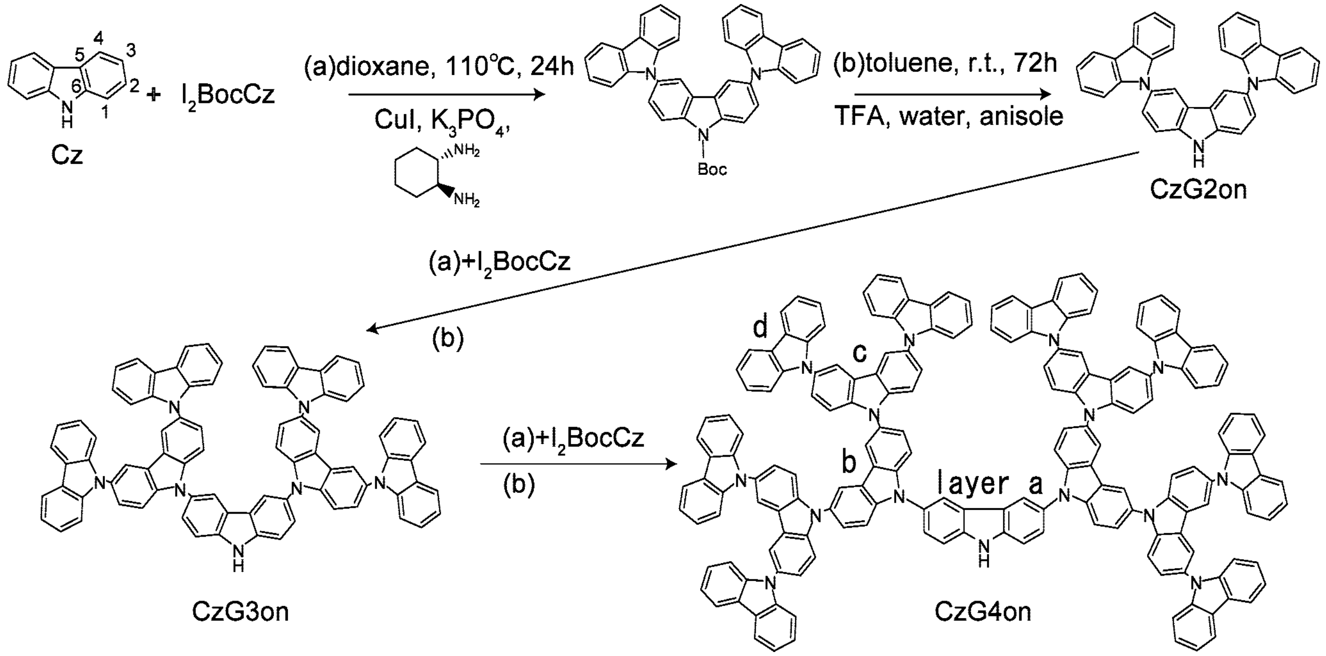
Scheme 3. Synthesis of Carbazole Dendrons, Numbering of the Carbazole Ring, and Naming of the Layers



when the generation increased from **G1Ph** to **G2Ph** due to the longer conjugation length. However, the red-shift of the absorption spectra was very small when the generation increased from **G2Ph** to **G3Ph** and not detected from **G3Ph** to **G4Ph**. Similarly, the fluorescence spectra have shown this same behavior, which indicates the limited conjugation length of the carbazole dendron and the highly twisted conformation (**CzG*n*on** showed the same behavior, see Figure S8). We postulate that this twisted conformation is mainly formed due to the steric hindrance of the planar conformation, and this assumption is exemplified by the fact that the molecular model of the planar G3 dendron has a steric overlap of the peripheral carbazoles (3D model of **CzG3on** optimized by a MOPAC (MM2) calculation (see Figure S9 in the Supporting Information).).[32]

The three results presented in this section show that the carbazole dendrons have a rigid backbone with a highly twisted structure. This structure causes a relatively limited conjugation length (only 2−3 layers), and this unique structure of the carbazole dendron has a strong relation to the expression of the potential gradient that will be described later.

3. Substituent Effect of Carbazole. To understand the electronic property of carbazole dendrons, understanding the substituent effect of the carbazole will be important because the electronic structures of the carbazole dendrons are based on the summation of the substituent effect of all the carbazoles. To study the substituent effect of carbazole, the NMR chemical shift of benzene, aniline,[33] and 9-phenylcarbazole[34] is shown in the Supporting Information (Figure S10). Amino groups are known as resonant electron-donating group, and the substituent effect of the amino group to benzene is clearly showing this (the overall upfield shift and the large difference of the chemical shift in the ortho and meta positions). On the other hand, the chemical shift of the carbazole substituted benzene shows a different behavior. The chemical shift of the ortho and para substituents shows a downfield shift and the values are very similar. This indicates that the resonance effect of the carbazole nitrogen is small, and a weak inductive electron-withdrawing effect exists. Fundamentally, the carbazole nitrogen atom is a strong electron donor with sp^2 hybridization.[30b] However, when the 9-phenyl ring has an antiplanar conformation, the conjugation (electron donation) of the carbazole ring to the 9-phenyl ring reduced significantly, and usually the 9-arylated carbazole compounds have an antiplaner conformation due to the steric hindrance of the 1,8-hydrogens and 2′,6′-hydrogens.[30a,35] On the basis of this explanation, the inductive electron-withdrawing effect of the 9-arylated carbazole groups due to the simple difference in the electronegativity of the carbon and nitrogen atoms can be explained. As was discussed in the last section, dendritic carbazoles have highly twisted structures due to the high steric hindrance. In this section, we will show that the inductive electron-withdrawing effect of the carbazole group exists in the carbazole dendrimers and suggest that the potential gradient is present in the dendritic backbone.

The HOMO levels of the carbazole dendrons (**G*n*Ph** and **G*n*B**) were electrochemically investigated. The DPV (differential pulse voltammetry) technique was used, and the HOMO level was estimated from the onset voltage of the oxidation.[19b,22a,f] The HOMO level (V vs vacuum level) of the carbazole dendrons are listed in Table 1. The HOMO level has a clear relation with the generation, i.e., when the generation of the carbazole increases, the HOMO level has increased. Further investigation of the electrochemical property was difficult due the common oxidative coupling reaction of the carbazole.[16a,b,19b] However, in a previous study of the 3,6-endcapped carbazole dendron (the coupling does not occur),[20d] it was reported that the oxidation of the carbazole dendron occurs from the outer layer. Therefore,

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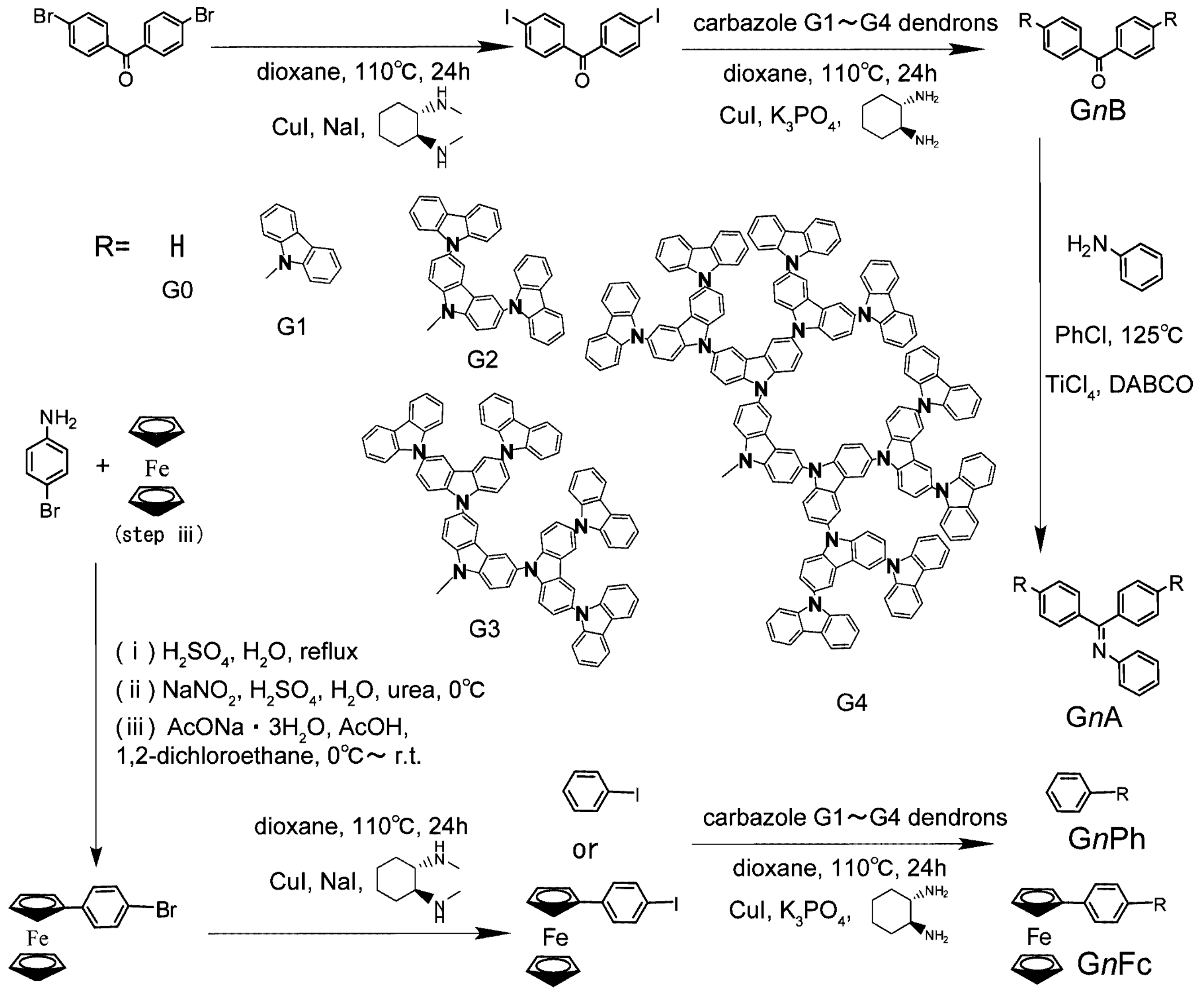
(32) The calculations were executed at the CAChe Worksystem ver. 5.04 (Fujitsu).

(33) SDBSWeb: http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology, May, 2008.).

(34) Bonesi, S. M.; Ponce, M. A.; Erra-Balsells, R. *J. Heterocycl. Chem.* **2004**, *41*, 161.

(35) Yu, H.; Zain, S. M.; Eigenbrot, I. V.; Phillips, D. *Chem. Phys. Lett.* **1993**, *202*, 141.

Scheme 4. Synthesis of Several Carbazole Dendron Substituted Compounds



this behavior of the HOMO level suggests that the electron density of the outer layer carbazole is increasing with the generation increase of the carbazole dendron.

The redox potential ($E^{1/2}$) of the carbazole dendron-substituted ferrocenes (**G*n*Fc**) were estimated by the cyclic voltammetry technique (CV) (Figures 4, and S11). All the ferrocene derivatives show a reversible and clear redox, and the redox potential was higher than of the unsubstituted 1-phenylferrocene (**G0Fc**). Because of the slight difference (few mV) in the redox potential of each generation, discussing the generation effect based on these data was difficult, but this indicates that the electron density of ferrocene has decreased, and the carbazole dendrons are working as an electron-withdrawing group.[27b,36]

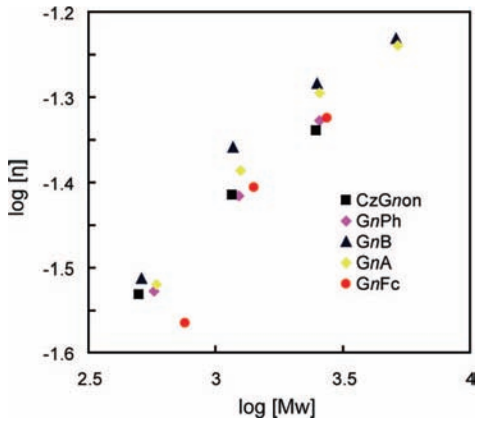


Figure 1. Mark–Houwink–Sakurada plot of carbazole dendron derivatives.

The relation of the benzophenone carbonyl frequency and the substituent effect in a carbon tetrachloride solution has been reported.[37] Therefore, the IR spectra of the carbazole dendron substituted benzophenones (**G*n*B**) were measured to study the details of the substituent effect of the carbazole dendrons. First, the vibration of the carbonyl group was detected in a carbon tetrachloride solution. However, the solubility of **G4B** was poor and the IR spectrum was undetectable in carbon tetrachloride. Therefore, the IR spectra of **G*n*B** were measured in a KBr pellet.

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(36) (a) Mason, J. G.; Rosenblum, M. *J. Am. Chem. Soc.* **1960**, *82*, 4206. (b) Little, W. F.; Reilley, C. N.; Johnson, J. D.; Sanders, A. P. *J. Am. Chem. Soc.* **1964**, *86*, 1382. (c) Kuwana, T.; Bublitz, D. E.; Hoh, G. *J. Am. Chem. Soc.* **1960**, *82*, 5811. (d) Hoh, G. L. K.; McEwen, W. E.; Kleinberg, J. *J. Am. Chem. Soc.* **1961**, *83*, 3949. (e) Hall, D. W.; Russell, C. D. *J. Am. Chem. Soc.* **1967**, *89*, 2316.

(37) Fuson, N.; Josien, M.-L.; Shelton, E. M. *J. Am. Chem. Soc.* **1954**, *76*, 2526.

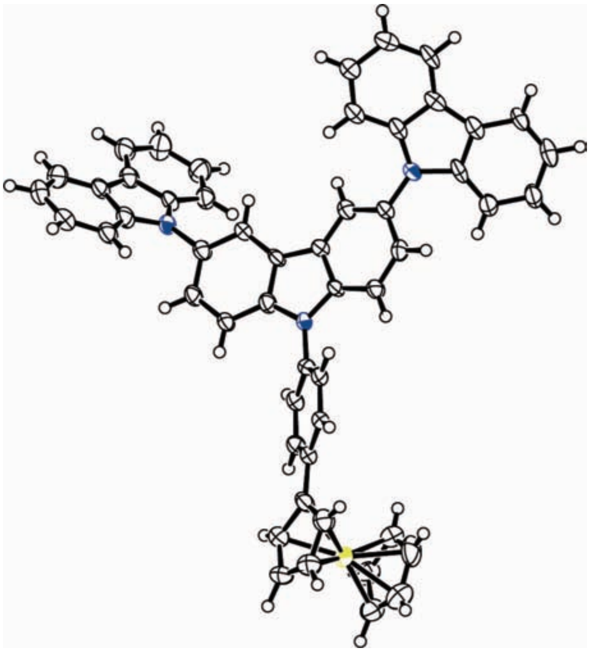

Figure 2. ORTEP diagrams of **G2Fc** with 50% probability. The bond radius is 0.06 Å, and the solvent molecule is removed.

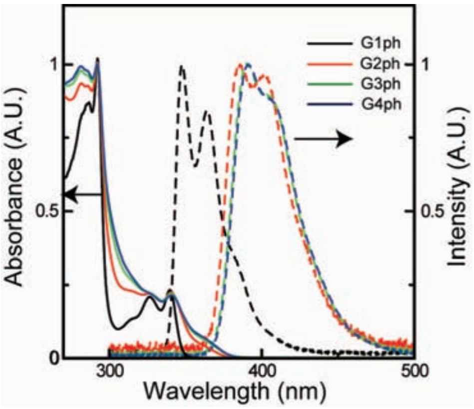

Figure 3. UV−vis absorption and fluorescence spectra of **G*n*Ph**. The solid lines are the UV−vis absorptions (THF solution), and the dotted lines are the fluorescence spectra (1 μ M THF solution). Both spectra are normalized at the strongest peak top.

Table 1. HOMO Level (eV) of **G*n*Ph** and **G*n*B**

compound	G1	G2	G3	G4
G*n*Ph	5.60	5.46	5.43	5.41
G*n*B	5.65	5.47	5.42	5.40

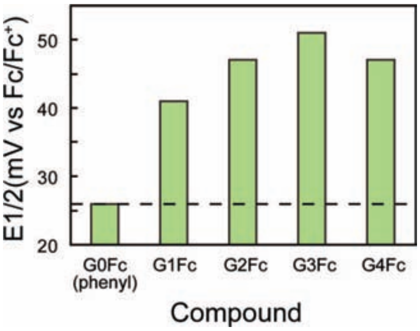

Figure 4. Redox potential ($E^{1/2}$) of **G*n*Fc**.

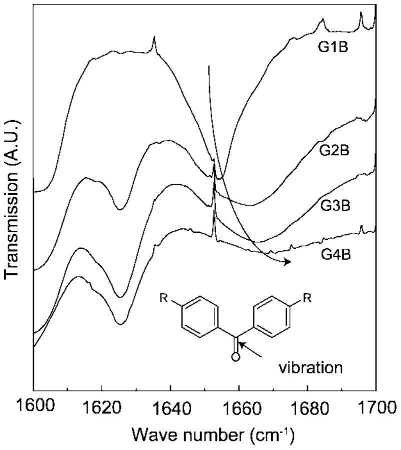

Figure 5. IR spectra of **G*n*B**.

The frequencies of the carbonyl groups of **G1B**, **G2B**, and **G3B** were the same as in carbon tetrachloride. Therefore, we used the frequency of the **G*n*B**s in the KBr pellet for the discussion (Figure 5). The carbonyl stretching frequency of **G1B** to **G4B** was 1654, 1664, 1667, and 1669 cm^{-1}, respectively. The carbonyl stretching frequency of simple benzophenone in carbon tetrachloride was 1663 cm^{-1}.[38] This indicates that in **G1B**, the carbazole dendron is working as an electron-donating substituent, and in higher generations, the carbazole dendrons are working as an electron-withdrawing substituent. As we discussed in the last section, **G1B** had a small dihedral angle between carbazole and benzene ring and this will increase the donating character of carbazole.[30] Therefore, the carbonyl stretching frequency of **G1B** showed a lower frequency. However, in higher generation carbazole dendrons, the carbonyl stretching frequency shifted to higher energy (higher than simple benzophenone) which means that the steric hindrance of the carbazole dendron induced the tilted structure and the carbazole dendron is working as an electron-withdrawing substituent. Additionally, the sequential shift indicates that the higher generation dendrons have stronger inductive electron-withdrawing effects,[39] i.e., the electron density of the inner-layer carbazole is decreasing when the generation increases due to the influence of the inductive electron-withdrawing effect of the outer-layer carbazoles.

Phenylazomethine derivatives form a complex with Lewis acids, and the coordination behavior has a relation with the electron density of the imine nitrogen.[14] To check the substituent effect of the carbazole dendrons, the coordination chemistry of the carbazole substituted phenylazomethines (**G*n*A**) were studied by UV−vis titration with $GaCl_3$.[40] Upon the addition of $GaCl_3$ to the **G*n*A** solution (benzene/acetonitrile = 4: 1), the spectra gradually changed with one isosbestic point (Figures 6, and S12). The titration curve of each **G*n*A** with the same concentration (50 μM) were drawn (Figure 7). As the curve shows, the equivalent amount of $GaCl_3$ that was needed until the spectra

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(38) SDBSWeb: http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology, November, 2008).

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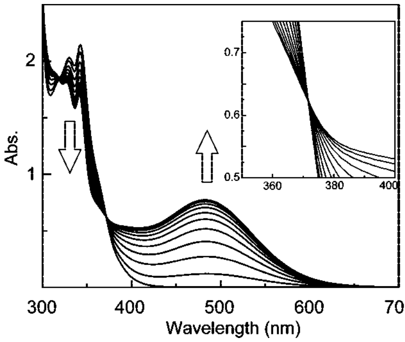

Figure 6. UV−vis spectra of **G2A** during the addition of $GaCl_3$ (solvent is benzene/acetonitrile = 4:1 and the concentration is 50 μM).

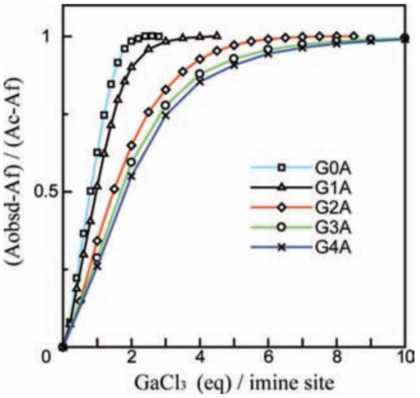

Figure 7. Titration curve of **GnA** (50 μM benzene/acetonitrile = 4:1 solution) with $GaCl_3$. Aobsd is the observed absorption, Af is the final absorption, and Ac is the commencement absorption.

change became saturated increased with increasing carbazole generation. This indicates a decrease in the binding constant between the imine and $GaCl_3$, i.e., the decrease of the electron density of the imine nitrogen atom. This behavior is similar to the frequency of the **G*n*B** and indicating that the inductive electron-withdrawing effect strengthens when the generation number of the carbazole increases.

All of these results in this section suggest that the carbazole dendrons have a generation-dependent inductive electron-withdrawing substituent effect. This also suggests that this effect products an inner layer electron-poor and outer layer electron-rich potential structure. However, the details of this potential gradient are still unclear on the basis of these results. In the next section, more specific details about the electron density will be described.

4. NMR Spectra of Carbazole Dendrons. In this section, the ^1H and ^{13}C NMR spectra of **G*n*Fc** will be presented and assigned to estimate the electron density of each layer of the carbazole dendrons. The ^1H NMR spectra of **G*n*Fc** ($n = 1-4$) are shown in Figure S13. Generally, the 4-position's (see scheme 3 for the numbering) proton of carbazole has a characteristic chemical shift (highest ppm of carbazole protons). Additionally, by using the integration value of these protons, the assignments of each layer's 4-position protons were done (pointed peaks in Figure S13). Interestingly, the chemical shift of the innermost layer has downfield shifted when generation of the carbazole increased, suggesting the lower electron density of the innermost layer. Similarly, the chemical shift of the outer to inner layer carbazoles (4-position) has sequentially shifted downfield, suggesting the outer layer electron-rich and inner layer electron-poor electronic structure.

By using the H−H COSY technique, the ^1H NMR spectra of **G*n*Fc** were completely assigned (Figures 8 and S14−16). The chemical shift of each proton in each layer has sequentially downfield shifted from the inner to outer layer. This result suggests that the electron density of the carbazole dendron gets sequentially higher from the inner to outer layer. However, the chemical shift of the ^1H NMR is easily influenced by the shielding effect and is difficult to relate it directly to the electron density. Therefore, the ^{13}C NMR spectra were next assigned using the C−H COSY and HMBC (heteronuclear multiple-bond connectivity) technique (Figures 9, and S17−22). Most of the ^{13}C NMR chemical shift of the same position in each layer showed a sequential upper or downfield shift. At the 3-positions, the outermost layer did not follow this trend because the carbazole substituent does not exist in the outermost layer, and in the 1- (layer b) and 4- (layer c) positions, one chemical shift showed an exceptional behavior. However, by applying these sequential changes (trend) in the chemical shift to recent reports that discusses the chemical shift and the electron density of the carbazole derivatives (the negative correlation of the electron density and ^{13}C NMR chemical shift are reported for the 2-position, i.e., the downfield shift indicates a higher electron density),[41] the substituent effect of the carbazole to carbazole can be explained as described in Figure 9. This result means that the substituent effect of the carbazole to carbazole is a π-polarization[42] type electron-withdrawing effect, i.e., when the carbazole binds to another carbazole, the entire π-electron cloud

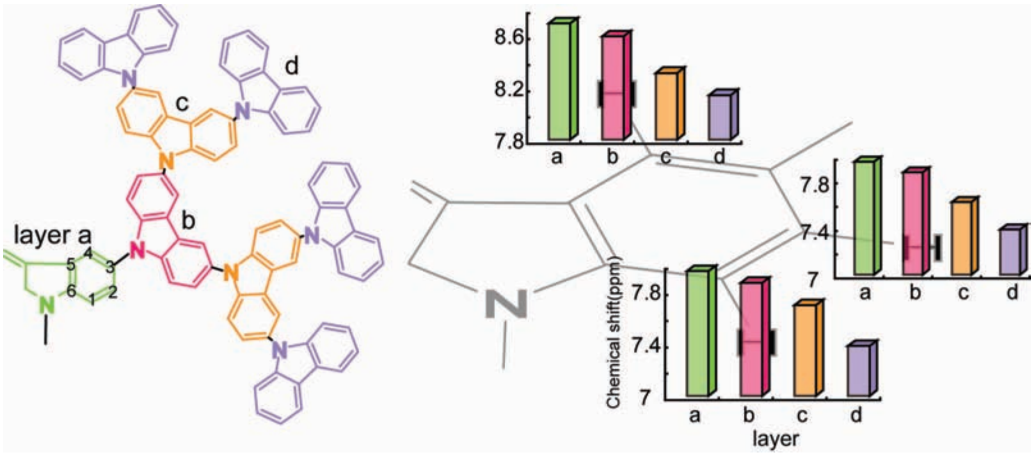

Figure 8. ^1H NMR chemical shifts of each layer (**G4Fc**).

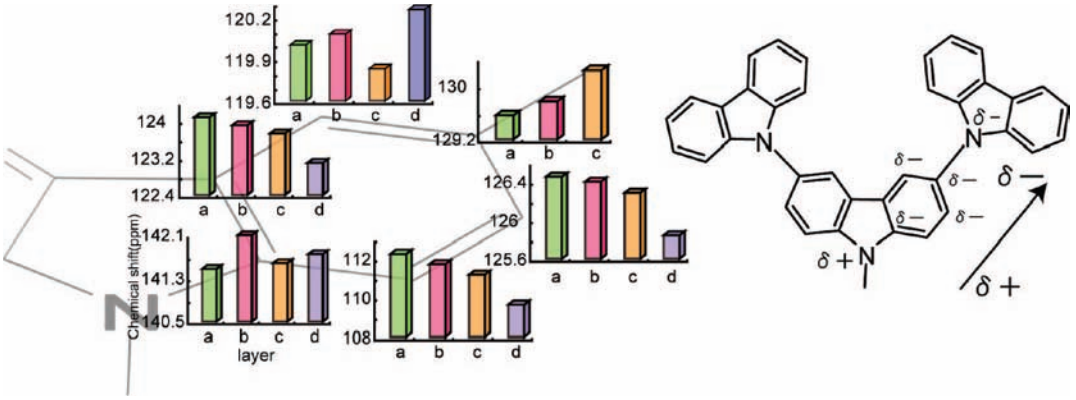

Figure 9. ^{13}C NMR chemical shifts of each layer (**G4Fc**) and the substituent effect of carbazole to carbazole that was derived from the chemical shifts.

is withdrawn from the outer layer carbazole. These trends in the ^{1}H and ^{13}C NMR chemical shifts were also observed in other generations (Figures S23 and 24), indicating that the consequence of this π-polarization produces a clear gradient of the electron density in the dendritic backbone. This result is supported by the calculated HOMO and LUMO orbital structures of **G*n*Ph** (see Figures S25−28 in the Supporting Information).[31] The calculated orbital showed an inner layer localized LUMO and the HOMO orbital structure such that the electron density is higher at the outer layer. Additionally, the Mulliken charge population of the carbazole nitrogen atom has sequentially decreased from the inner to outer layer, indicating the outer layer electron-rich potential gradient (see Table S1 in the Supporting Information).

In this section, the complete assignment of the ^{1}H and ^{13}C NMR was done and the mechanism and the existence of the potential gradient in the carbazole dendrimer were revealed. This electron density gradient means that the potential (HOMO) level of the outer layer is higher than the inner layer, and the three-dimensional potential gradient is present in the dendritic carbazole backbone.

Conclusion

In conclusion, a new synthesis of carbazole dendrimers was developed and several derivatives were synthesized. Through the measurement of the substituent effect of the carbazole dendrons, the inductive electron-withdrawing substituent effect of the carbazole dendron induced by the highly twisted structure was discovered. Finally, with the complete assignment of the ^{1}H and ^{13}C NMR spectra, the existence of the outer layer electron-rich three-dimensional potential gradient in the carbazole dendron was revealed. This new material with a potential gradient should show unique functions in several devices or systems that involve electron transfer. However, the discovery of the potential gradient and mechanism has a more significant fundamental meaning, i.e., as the first step to allow the full control and design of the intramolecular potential structure.

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Note Added after ASAP Publication. Figure 9 was incorrect in the version published ASAP on January 28, 2009; the correct version published on the web on February 11, 2009.

Supporting Information Available: Experimental section, calculated structures, NMR charts, crystal structure determination section, cif files, and several additional data. This material is available free of charge via the Internet at http://pubs.acs.org.

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