## Synthesis of Phenylacetylene Dendrimers Having Sterically Congested Diazo Units and Characterization of Their Photoproducts

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The compound (4-tert-butyl-2,6-dimethylphenyl)(2,4,6-tribromophenyl)diazomethane (1a), a precursor for persistent triplet carbene, was found to be stable enough to survive Sonogashira coupling reaction conditions to give (4-tertbutyl-2,6-dimethylphenyl)(2,6-dibromo-4-ethynylphenyl)diazomethane (2a). The diazomethane 2a was used as a starting compound for synthesis of phenylacetylene dendritic molecules having peripheral diazo groups by the convergent method. Thus, tridendrons with peripheral groups bearing 3 (3a), 6 (6a), and 12 (8a) diazo units were prepared, in which diazo groups were introduced so as to generate polycarbenes in a ferromagnetic fashion. In order to characterize the spin

There has been an ever-increasing interest in molecular magnetism, in which spins of unpaired electrons in  $\pi$ -orbitals of light atoms, such as carbon, nitrogen, and oxygen, are mainly responsible. Actually, many attempts have been made to prepare organic ferromagnetic materials.<sup>[1,2]</sup> Spin sources used for such studies are mostly thermodynamically stable radicals, such as galvinoxyls,<sup>[2g]</sup> triphenylmethyls,<sup>[3a]</sup> and nitroxides,<sup>[3b]</sup> mostly because of their ease of preparation and application. Potential problems emerge for these radicals, for instance, the exchange coupling between the neighboring nitroxides is weak. Triplet carbenes are regarded as one of the most effective spin sources since the magnitude of the exchange coupling between the neighboring centers is large.<sup>[4,5]</sup> Moreover, the photolytic production of polycarbenes is possible in solid solution at cryogenic temperatures if poly(diazo) precursors are available. Iwamura and co-workers have prepared a "starburst-"type nona(diazo) compound and have demonstrated that nine diazo groups are photolyzed at low temperature to give a nonadecet ground state (S = 9).<sup>[5]</sup>

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states of carbenes generated by the photolysis of these dendrimers, the magnetic susceptibility of the photoproducts was measured. Although the data for the photoproduct of the tris(diazo) compound were fitted with S = 2.5, those for the photoproducts of hexakis and dodecakis(diazo) compounds were fitted with S = 1.62, a value that is much smaller than the theoretically predicted value and even smaller than that of triscarbene. The results are interpreted in terms of the disjoint-nondisjoint concept.

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However, those systems have two disadvantages that hinder their further use in magnetic materials. First, a triplet carbene unit is highly unstable for practical applications under ambient conditions. In order to overcome these difficulties, we have made great efforts to stabilize and hopefully isolate the triplet carbene and have succeeded in preparing fairly stable carbenes that survive for hours in solution at room temperature.<sup>[6]</sup> The next step is to explore a way to connect them while retaining a robust  $\pi$ -spin polarization. The second disadvantage that arises is that diazo groups are also generally labile<sup>[7]</sup> and, hence, are usually introduced at the last step of synthesis.<sup>[5]</sup> In other words, the diazo compound cannot be used as a building block to prepare a more complicated poly(diazo) compound, and, thus, the synthesis of the precursor diazo compounds becomes more difficult and laborious as the number of diazo units increases. We found, almost accidentally, that a diphenyldiazomethane prepared to generate a persistent triplet carbene is also persistent for the diazo compound and, hence, can be further modified with the diazo group intact into a more complicated diazo compound. For instance, bis(2,4,6-tribromophenyl)diazomethane is found to be stable enough to survive Sonogashira coupling reaction conditions and undergoes a coupling reaction with trimethylsilylacetylene to bis(2,6-dibromo-4-trimethylsilylethynylphenyl)diazogive methane. Three units of the diazo compound are then introduced at the 1-, 3-, and 5-positions of the benzene ring through the ethynyl group by employing a similar coupling reaction to give a tris(diazo) compound, which eventually

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generates a fairly stable septet ground state triscarbene upon irradiation.<sup>[8]</sup>

These results suggest that the diazo compound can be used as a building block to prepare a poly(diazo) compound, which then can generate a high-spin polycarbene with considerable thermal stability. One way to realize this is to prepare phenylacetylene dendrimers having sterically congested diazo units. We report here our efforts to prepare such dendrimers and to characterize the oligocarbenes generated from those precursor oligo(diazo) compounds.

### **Results and Discussion**

#### **Design of Precursor Dendrimers**

There is a simple way to predict the ground-state multiplicity of alternant hydrocarbons. For instance, Ovchinnikov has derived a method of predicting the ground-state multiplicity of alternant hydrocarbons based on valence bond theory by counting starred and unstarred carbon atoms.<sup>[9]</sup> His conclusion is expressed in terms of Equation (1):

$$S = (n^* - n)/2$$
(1)

where  $n^*$  and n are the number of starred and unstarred carbon atoms, respectively. When triplet carbones that have the spin quantum number S = 1 are used as spin sources, Equation (1) can be rewritten as follows [Equation (2)]:

$$S = n^* - n \tag{2}$$

If this method is applied to design dendrimers having diazo units so as to generate polycarbenes with a high-spin ground state by using a Sonogashira coupling reaction, the simplest way is to introduce the precursor diazo unit on a benzene ring in a *meta* fashion. For instance, in dendritic triscarbene A in Scheme 1, the numbers of starred and unstarred carbon atoms are 18 and 15, respectively, and hence, S = 3 is predicted. Similarly, for dendrimers having 6 and 12 carbene units (B and C in Scheme 1, respectively) at the terminal points, S = 6 and 12 are predicted, respectively. Thus, the preparation of the precursors for those carbenes are executed.

# Preparation of Phenylacetylene Dendrimers with Peripheral Diazo Groups

Methods for synthesis of phenylacetylene dendritic macromolecules have been developed.<sup>[10]</sup> The divergent method is shown to be hampered by the poor solubility of the growing macromolecules,<sup>[10,11]</sup> and it also requires



Scheme 1

rather drastic conditions for the synthetic cycle to be completed. For example, the iodine-promoted deprotection of 1-aryl-3,3-dialkyltriazenes to the corresponding aryl iodide is carried out at 90–110 °C in a sealed tube.<sup>[12]</sup> The convergent method is shown to possess several advantages over the divergent method. Above all, the synthetic cycle can be completed under very mild conditions.<sup>[10,11]</sup> This is especially important for constructing a dendrimer carrying a chemically sensitive functional group such as a diazo group.

The compound (4-tert-butyl-2,6-dimethylphenyl)(2,4,6tribromophenyl)diazomethane (**1a**) is selected as a starting diazo precursor for the following reasons. First, it is expected to survive the chemical manipulations required to introduce a proper functional group in order to modify it to a "monodendron", since the diazo carbon is wellshielded by four relatively bulky groups at the *ortho* positions. Secondly, it is also expected to generate a fairly persistent triplet carbene upon photoexcitation as it has been shown that bis(2,4,6-tribromophenyl)diazomethane generates the corresponding triplet carbene which survives minutes in solution and months in a crystalline state at room temperature.<sup>[6,8]</sup> Finally, alkyl groups, i.e. methyl and *tert*- butyl groups, on one side of phenyl ring in **1a** are expected to both protect the carbonic center and also improve solubility, which will become a serious problem at higher generations.

The desired diazomethane **1a** was prepared starting from 2,4,6-tribromobenzaldehyde by the procedures outlined in Scheme 2. It was easily purified either by silica gel column chromatography at -5 °C or by repeated chromatography on a gel permeation column to give a rather stable orange solid, which could be stored in a refrigerator at -10 °C for several months without any appreciable decomposition. The remarkable thermal stability of **1a** was shown by its high melting point; it decomposed at 117 °C.

The diazomethane **1a** was also found to be stable enough to survive Sonogashira coupling reaction conditions in the presence of Pd<sup>0</sup> and CuI (Scheme 3).<sup>[13]</sup> Thus, treatment of **1a** with trimethylsilylacetylene in the presence of (Ph<sub>3</sub>P)<sub>2</sub>PdCl<sub>2</sub> and CuI in NEt<sub>3</sub> for one day at 40 °C, followed by gel permeation chromatography (GPC), gave (2,6dibromo-4-trimethylsilylethynylphenyl)(2,6-dimethyl-4-*tert*butylphenyl)diazomethane (**2a**-TMS) in a 50–60% yield. The presence of intact diazo functional groups in the prod-



ucts was unequivocally shown by the presence of strong, sharp bands at 2053 cm<sup>-1</sup> assigned to the diazo stretching vibration in the IR spectra. These observations clearly indicate that the diazo group in **1a** is remarkably resistant toward metal halides, which usually catalyze the decomposition of diazoalkanes.<sup>[14]</sup>

The deprotection<sup>[15]</sup> of the trimethylsilyl group in **2a**-TMS proceeded equally smoothly by treating it with NaOH and *t*BuOH at room temperature, and the diazo group remained intact to give (2,6-dibromo-4-ethynyl-phenyl)(2,6-dimethyl-4-*tert*-butylphenyl)diazomethane (**2a**). Before converting **2a** into the zero-generation mono-dendron by reacting it with an appropriate difunctional monomer, we coupled it with 1,3,5-triiodobenzene. The triiodobenzene was chosen as a linker in which three carbene precursor units are properly introduced so as to generate triscarbene connected in a ferromagnetic fashion. The coupling reaction proceeded smoothly under mild conditions to form 1,3,5-tris{2-[3,5-dibromo-4-(4-*tert*-butyl- $\alpha$ -diazo-2,6-dimethylbenzyl)phenyl]ethynyl}benzene (**3a**) in 50% yield.

The characterization of the tris(diazo) compound **3a** was mainly based on <sup>1</sup>H NMR and IR spectroscopy. The <sup>1</sup>H NMR spectrum of **3a** shows two singlets ( $\delta = 1.31$  and 2.18 ppm) corresponding to the *tert*-butyl and methyl groups, respectively, and three aromatic singlets ( $\delta = 7.10$ , 7.62, and 7.74 ppm) in the ratio of 3:2:2:1:2, in agreement with the calculated value. A strong, sharp band at 2048 cm<sup>-1</sup> is observed in the IR spectrum. However, molecular weight determination by using MS, which is conventionally employed to characterize dendrimers, could not be used in the present system since the diazo functional groups could not survive the ionization processes. One way to solve this problem is to convert all the diazo groups in 3a to a stable functional group and to determine the molecular weight of the resulting trimeric product. This sounded reasonable since there are several ways to quantitatively convert diazo groups to other functional groups; these include the treatment with hydrochloric acid to give the corresponding chloride and photolysis in methanol to give the methyl ether as a result of O–H insertion of the photogenerated carbene into the solvent.<sup>[14]</sup> However, all attempts to convert **3a** cleanly into a tris compound with a stable functional group were unsuccessful. This is obviously due to the highly congested nature of its reaction centers.

Therefore, we decided to prepare an authentic sample. Tris(ketone) **3b** was prepared following essentially the same reaction procedure as outlined in Scheme 2 with the use of (4-*tert*-butyl-2,6-dimethylphenyl)(2,4,6-tribromophenyl)-ketone (**1b**) as a starting compound. Matrix-assisted laser desorption ionization time-of-flight MS (MALDI-TOF MS) of the ketone **3b** affords a M<sup>+</sup> ion peak at 1410 (1:1 CH<sub>3</sub>OH/CHCl<sub>3</sub>, positive mode). The spectrum for the M<sup>+</sup> ion cluster from the high-resolution spectrum exhibits isotopic distributions essentially identical to those simulated for C<sub>69</sub>H<sub>60</sub>Br<sub>6</sub>O<sub>3</sub> (Figure S1). The fully characterized trisketone **3b** was then used as "standard" in the analysis of the diazo counterpart by GPC. The elution volume of **3a** was actually found to be in complete agreement with that of **3b** (Figure S4).

Encouraged by these findings, we started to prepare a zero monodendron by treating 2 equivalents of 2a with a



#### Scheme 4

difunctional monomer. 2-(3,5-Diiodophenyl)-1-(trimethylsilyl)acetylene (4)<sup>[16]</sup> was selected for the convergent synthesis. This monomer is easily prepared<sup>[16]</sup> in good yield from 1,3,5-triiodobenzene. Scheme 4 and Scheme 5 illustrate the chemistry used in preparing phenylacetylene dendrimers containing 6 (**6a**) and 12 (**8a**) diazo units by the convergent approach. The synthesis begins with the preparation of a series of monodendrons (**5a** and **7a**) using a repetitive process. Thus, coupling of the aromatic diiodide **4** with 2 equivalents of a terminal alkyne **2a** carrying a persistent triplet carbene precursor resulted in the formation of a zero-generation monodendron (**5a**-TMS) in 86% yield. The product was easily separated from the oxidative dimer and the mono-substituted product by GPC. The dendron was then deprotected under basic conditions to give a terminal alkyne **5a** at the monodendron focal point. Two equivalents of **5a** were then coupled with monomer **4** followed by the deprotection to give the first-generation (n = 1) product **7a** bearing four peripheral diazo units in 72% yield.

Instead of continuing the repetitive process further, we coupled the zero- and first-generation monodendrons (**5a** and **7a**, respectively) to a core, i.e. 1,3,5-triiodobenzene. The coupling took place very smoothly to produce phenylacety-lene dendrimers having 6 (**6a**) and 12 (**8a**) diazo units in 79 and 60% yields, respectively, where six and twelve diazo units are aligned so as to generate hexakis- and dodecakis-carbene in a ferromagnetic fashion. The coupling reactions



were always accompanied by the formation of small amounts of partially substituted products and symmetrical diacetylenes, but the desired dendrimers were easily separated from those by-products by GPC.

Proton NMR spectroscopy was found to be useful for the characterization of the dendrimers to a first approximation. The assignments are based on the integral ratio of the prominent protons, i.e. *tert*-butyl, methyl, and aromatic protons, which were well resolved to make relatively precise measurements possible. For instance, the <sup>1</sup>H NMR spectrum of **6a** shows two singlets ( $\delta = 1.31$  and 2.17 ppm) corresponding to the *tert*-butyl and methyl groups, respectively, with a ratio of 3:2, and five aromatic protons [ $\delta =$ 7.10 (s), 7.63 (t), 7.65 (d), 7.68 (s), and 7.75 (s)] with the ratio of 4:1:2:1:4. The presence of a sharp, strong band at 2054 cm<sup>-1</sup> in the IR spectrum of **6a** and **8a** again indicates that the diazo functional group remains intact during the processes.

In order to determine the molecular weight of the dendrimers indirectly, again we prepared the corresponding ketone dendrimers as a standard for GPC analysis. The desired dendrimers (**6b** and **8b**) were prepared according to essentially the same procedures as outlined in Schemes 4 and 5, except that the corresponding ketone **2b** was used in place of **2a**. The molecular weight of the ketone dendrimers determined by MS was found to be consistent with those expected for the structure (Figures S2 and S3).<sup>[17]</sup> Those fully characterized "authentic" dendrimers were then used as a standard for GPC analysis, and excellent agreement of the elution volume between the ketone and diazo dendrimers (Figure S4) was observed.

# SQUID Measurements of Photoproducts from Dendrimers (3a, 6a, and 8a)

In order to characterize the spin states of carbenes generated by photolysis of the dendrimers, the following measurements were carried out.

Photolysis of 3a in 2-methyltetrahydrofuran (2-MTHF) at 77 K in an X-band ESR cavity resulted in the appearance of single-line signals centered at around 330 mT (Figure 1). Although the spectral features are very different from that observed in the photolysis of the corresponding monodiazomethane (1a or 2a), it was difficult to simulate the spec-



Figure 1. ESR spectra obtained by irradiation of tris(diazo) compound **3a** in 2-methyltetrahydrofuran at 77 K

tra because the line widths were broader than the simulated line spacings. The signal spacing was so small that no fine structures were observed. This is consistent with the observation that the higher the spin multiplicities are, the smaller the D values become.<sup>[18]</sup> Thus, it was very difficult to identify the spin states of triscarbene unequivocally from conventional X-band ESR spectroscopy.

In order to determine the spin states of the photoproducts from **3a**, the magnetic susceptibility of the photoproduct was measured. Thus, the 2-MTHF solution of the tris-(diazo) compound **3a** (0.5 mM) was placed inside the sample compartment of a Superconducting Quantum Interference Device (SQUID) magnet/susceptometer and irradiated with light ( $\lambda = 488$  nm) from an argon ion laser through an optical fiber at 5–10 K. The magnetization for **3a** at 5 K in a constant field of 5 kOe was monitored in situ with respect to irradiation time and is shown in Figure 2a. As the irradiation time increased, the *M* values gradually increased as well and reached a plateau after several hours. The magnetization before and after irradiation,  $M_b$  and  $M_a$ , respectively, were measured at 2 and 5 K in a field range of 0–50



Figure 2. (a) Plot of magnetization (*M* in emu) as a function of irradiation time observed in the photolysis of tris(diazo) compound **3a** in 0.5 mM 2-methyltetrahydrofuran matrix measured at 5.0 K and 5 kOe; (b) field dependence of the magnetization of the photoproduct from tris(diazo) compound **3a** in 0.5 mM 2-methyltetrahydrofuran matrix measured at 2.0 and 5.0 K;  $M_b$  and  $M_a$  refer to the magnetization value before and after irradiation, respectively, and  $M = M_a - M_b$ 

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kOe. The paramagnetic contribution was then obtained by subtracting the corresponding values obtained before and after irradiation (Figure 2b). The effect of any paramagnetic impurities can be cancelled by this treatment. The plots of the magnetization  $(M = M_a - M_b)$  versus the temperature-normalized magnetic field (H/T) were analyzed in terms of the Brillouin function as follows:<sup>[1c,5,19]</sup>

$$M = M_{\rm a} - M_{\rm b} = FNgJ\mu_{\rm B}B(\chi) \tag{3}$$

where  $B(\chi) = [(2J + 1)/2J] \cdot \coth\{[(2J + 1)/2J] \cdot \chi\} - [1/2J] \cdot \coth(\chi/2J)$  and  $\chi = Jg\mu_B H/k_B T$ . *F* is the photolysis factor of diazo compounds, *N* is the number of the molecule, *J* is the quantum number for the total angular momentum,  $\mu_B$  is the Bohr magneton, *g* is the Landé *g*-factor, and  $k_B$  is the Bohr magneton. Since these carbenes are constituted of light elements, the orbital angular momentum should be negligible, and *J* can be replaced with spin quantum number *S*.

The M/Ms versus H/T plots are shown in Figure 3, together with theoretical curves with S = 1, 2, and 3.<sup>[20]</sup> The observed data (M vs. H/T) for the photoproduct of the tris-(diazo) compound **3a** closely traced the theoretical curve with S = 3. The data were fitted with Equation (3) with S = 2.4 and F = 1.05. The value is somewhat smaller than the theoretically predicted value of 3, but indicates that the three carbene centers interact ferromagnetically. Since the magnetization data at two different temperatures were fitted to the same Brillouin function, the sample is considered to be free from ferro- or antiferromagnetic intermolecular interactions and the septet state is considered to be a ground state.



Figure 3. Plot of magnetization normalized by saturation magnetization (*Ms*) obtained upon photolysis of tris(diazo) compound **3a** measured at 2.0 and 5.0 K vs. temperature-normalized magnetic field (*H*/*T* in kOe K<sup>-1</sup>); theoretical curves with S = 1, 2 and 3 are also indicated

Similar measurements were made for the photoproducts from hexakis- (6a) and dodecakis(diazo) compounds (8a), and the data are shown in Figure 4 and Figure 5, respectively, with theoretical curves with S = 1, 2 and 3. The data

traced the theoretical curve with a very low *S* value. The experimental data (*M*/*Ms* vs. *H*/*T*) were fitted best with Equation (3) with  $S = 1.62 \pm 0.01$ ,  $F = 2.85 \pm 0.03$  for the hexakis(diazo) compound and  $S = 1.62 \pm 0.01$ ,  $F = 3.35 \pm 0.04$  for the dodecakis(diazo) compound. Thus, the values are disappointingly smaller than the theoretically predicted values, S = 6 and 12 for **6c** and **8c**, respectively, even smaller than that of triscarbene **3c**.



Figure 4. Plot of magnetization normalized by saturation magnetization (*Ms*) obtained upon photolysis of hexakis(diazo) compound **6a** measured at 2.0 and 5.0 K vs. temperature-normalized magnetic field (*H*/*T* in kOe K<sup>-1</sup>); theoretical curves with S = 1, 2 and 3 are also indicated



Figure 5. Plot of magnetization normalized by saturation magnetization (*Ms*) obtained upon photolysis of dodecakis(diazo) compound **8a** measured at 2.0 and 5.0 K vs. temperature-normalized magnetic field (*H*/*T* in kOe K<sup>-1</sup>); theoretical curves with S = 1, 2 and 3 are also indicated

The reason for the apparent smaller values may be due to the incomplete decomposition of the diazo functional groups. To confirm this, the UV/V spectra of the diazo compounds before and after the magnetic measurements were recorded. The rate of the photolysis could be monitored by observing the  $n-\pi^*$  absorption band. The degree of the photolysis was completed to be >95% on the whole (Figure S5).

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Other factors that should be taken into account are the inter- and/or intramolecular antiferromagnetic interactions, as these interactions are known to reduce the effective mag-

netic moment. The magnitude of the exchange coupling between the spins is dependent upon the structure of the linkers,<sup>[21]</sup> and the magnitude decreases as the number of



### Scheme 8

the intervening benzene rings increases, indicating that polarization of the  $\pi$ -electrons on the benzene rings gradually attenuates as the length between the radical sites increases. If this value is not large, the antiferromagnetic interaction becomes important, especially at low temperature.

The results can be more reasonably interpreted in terms of the disjoint-nondisjoint concept based on MO theory.<sup>[22,23]</sup> Borden and Davidson<sup>[23]</sup> noted that the localizability of the Hückel nonbonding molecular orbitals (NBMO) is crucial in governing the ground states of non-Kekulé hydrocarbon diradicals. When the degenerate Hückel nonbonding molecular orbitals have no atoms in common, a situation that is known as "disjoint" arises, and there is no probability that both electrons will simultaneously occupy the same AO. Thus, to a first approximation, the lowest singlet and the lowest triplet states have the same energy. Since dynamic spin polarization<sup>[24]</sup> between the two electrons with an opposite spin is important in the singlet state in this case, the singlet state becomes a ground state. On the other hand, when NBMOs have atoms in common, a situation that is described as "non-disjoint" arises, and a triplet ground state is expected since in this state the Pauli principle prevents the two electrons in the NBMOs from simultaneously appearing in the AOs that the two NBMOs have in common.

By applying this theory to our molecules, it can be explained why triscarbene 3c has a triplet state as the Ovchinnikov rule predicts, while hexakis- and dodecakiscarbenes have lower spin states than predicted. Thus, in the case of the triscarbene, the three carbene units are connected to a central benzene ring in a non-disjoint manner to afford a high-spin ground state (Scheme 6). On the other hand, hexakis 6c consists of a dendritic structure, which has a biscarbene unit at the terminal branches. The connectivity of two carbene units within this biscarbene unit is non-disjoint and, hence, they interact in a ferromagnetic fashion with spin quantum number S = 2. However, the connectivity between three biscarbene units through the central benzene ring is disjoint (Scheme 7). Consequently, each energy level of these disjoint systems is nearly degenerate. Similarly, while the connectivity of two carbene units within the biscarbene unit at the terminal branches in dodecakiscarbene is disjoint to generate the S = 2 spin state, the connectivity between six biscarbene units through the core part is disjoint. Thus, there are no magnetic interactions between the biscarbene units through the core part in hexakis- and dodecakiscarbene.

On the other hand, the large F values, 2.85 and 3.35, observed for the photoproducts from **6a** and **8a**, respectively, indicate that more than one unit of the S = 1.62 spin states are formed from one mol of the diazo compounds. In other words, hexakiscarbene **6c** is regarded as a species comprising of 2.85 units of S = 1.62 spin state, while dodecakiscarbene **8c** is a species having 3.35 units of S = 1.62 spin state. These are roughly in agreement with the spin situation illustrated in Scheme 7 and Scheme 8.

### Conclusion

The present research has revealed that the convergent method for the synthesis of phenylacetylene dendritic molecules can be applied to prepare tridendrons having peripheral diazo functional groups. The poly(diazo) dendrimers thus prepared generated polycarbenes cleanly and efficiently upon photoirradiation. Although triscarbene was shown to have a septet ground state, as was expected, polycarbenes from higher-generation poly(diazo) compounds were found to have a lower spin state of S = 2 probably because of the disjoint connectivity between exterior and interior parts. This may mean that the present method is not useful for the preparation of high-spin polycarbenes. However, the connectivity will be improved by introducing a spin unit on the core ring that disrupts the magnetic interaction between the spin units at the branches. A simple way to realize this is to introduce a stable radical unit on a core benzene.

Thus, it is potentially possible to extend the synthesis afford larger dendritic molecules, which can generate highspin magnetic species upon photoirradiation. One of the benefits from the high level of molecular precision has been suggested to lie in the area of single-molecule electronic or photonic devices.<sup>[2]</sup> The existence of large dentritic molecules with spin functionality will open a new window for materials science.

### **Experimental Section**

General Information: IR spectra were measured on a JASCO FT/ IR-410 spectrometer, and UV/Vis spectra were recorded on a JA-SCO V-560 spectrometer. The mass spectra were recorded on a JEOL JMS-600H mass spectrometer and Voyger DE-PRO MALDI-TOF mass spectrometer. <sup>1</sup>H (300 MHz) and <sup>13</sup>C (75 MHz) NMR spectra were determined with JEOL JNM-AL300 FT/ NMR spectrometer in CDCl3 with Me4Si as an internal reference. The magnetic measurements were done on a 5-T Quantum Design MPMS SQUID magnetometer. Thin-layer chromatography was performed on Merck Kieselgel 60 PF254. Column chromatography was carried out on a silica gel (Merck for dry column chromatography) or on an aluminum oxide, active neutral (activity I) (ICN for column chromatography). GPC was performed with a JASCO PU-986 chromatograph with a UV-970 UV/Vis detector using a Shodex GPC H-2001 (20 mm  $\times$  50 cm) or GPC H-2002.5  $(20 \text{ mm} \times 50 \text{ cm})$  column.

**Preparation of (4**-*tert*-**Butyl-2,6**-**dimethylphenyl)(2,4,6**-**tribromophenyl)diazomethane (1a):** One-tenth of a solution of 2-bromo-5*tert*-butyl-1,3-dimethylbenzene<sup>[25]</sup> (7.2 g, 30 mmol) in anhydrous Et<sub>2</sub>O (15 mL) was added to a mixture of magnesium ribbon (0.8 g, 33 mmol) and a crystal of iodine in anhydrous Et<sub>2</sub>O (10 mL), and the mixture was sonicated for 1 h. The residual part of the bromide solution was added dropwise and the mixture was refluxed overnight. After cooling at 0 °C, a solution of 2,4,6-tribromobenzaldehyde<sup>[26]</sup> (10.3 g, 30 mmol) in anhydrous THF (25 mL) was added to the Grignard reagent, and the mixture was refluxed for 5 h. A saturated NH<sub>4</sub>Cl solution was added carefully and the mixture was extracted with Et<sub>2</sub>O. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and the solvents evaporated to leave a crude product, which was purified by silica gel column chromatography eluted with CHCl<sub>3</sub>/n-hexane (1:1). (4-tert-Butyl-2,6-dimethylphenyl)-(2.4.6-tribromophenyl)methanol was obtained as a white solid in 36% yield. M.p. 91.5–93.4 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta =$ 1.29 [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>], 2.26 (s, 6 H, CH<sub>3</sub>), 2.60 (d,  ${}^{3}J$  = 8.82 Hz, 1 H, OH), 6.40 [d,  ${}^{3}J$  = 8.82 Hz, 1 H, ArCH(OH)Ar], 6.97 (s, 2 H, ArH), 7.72 (s, 2 H, ArH) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta =$ 21.7 (CH<sub>3</sub>), 31.2 [C(CH<sub>3</sub>)<sub>3</sub>], 34.1 [C(CH<sub>3</sub>)<sub>3</sub>], 76.3 [ArCH(OH)Ar], 121.3 (Ar), 124.8 (Ar), 126.9 (Ar), 133.9 (Ar), 136.1 (Ar), 136.6 (Ar), 139.6 (Ar), 150.6 (Ar) ppm. MS: m/z (%) = 508 (M + 6, 5.0), 506 (M +4, 14.1), 504 (M +2, 14.6), 502 (4.8) [M<sup>+</sup>], 343 (30.2), 57 (100). HRMS for  $C_{19}H_{21}OBr_3$ : calcd. 501.9141; found 501.9136. A solution of the methanol (5.5 g, 11 mmol) and SOCl<sub>2</sub> (20 mL) was stirred at room temperature for 2 days and the solvents were evaporated under reduced pressure to give (4-tert-butyl-2,6-dimethylphenyl)(2,4,6-tribromophenyl)chloromethane as a brown semisolid in 99% yield: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 1.28$ [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>], 2.38 (s, 6 H, CH<sub>3</sub>), 6.84 [s, 1 H, ArCH-(Cl)Ar], 6.97 (s, 2 H, ArH), 7.74 (s, 2 H, ArH) ppm. <sup>13</sup>C NMR  $(75 \text{ MHz}, \text{CDCl}_3): \delta = 22.8 (\text{CH}_3), 31.1 [C(CH_3)_3], 34.0 [C(CH_3)_3],$ 62.0 [ArCH(Cl)Ar], 122.1 (Ar), 125.7 (Ar), 127.2 (Ar), 130.9 (Ar), 136.4 (Ar), 137.2 (Ar), 137.6 (Ar), 150.6 (Ar) ppm. A mixture of silver tetrafluoroborate (2.5 g, 13 mmol), ethyl carbamate (13.5 g, 152 mmol), and 1,4-dioxane (20 mL) was heated at 60 °C. A solution of the chloride (5.7 g, 11 mmol) in dioxane (30 mL) was added, and the mixture was heated overnight at 100 °C. The mixture was filtered, and water (30 mL) and CHCl<sub>3</sub> (30 mL) were added to the filtrate. The organic layer was washed well with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. A brown oil obtained after concentration of the solution was chromatographed on a silica gel column eluted with CH<sub>2</sub>Cl<sub>2</sub>/n-hexane (2:1). Ethyl N-[(4-tert-butyl-2,6-dimethylphenyl)(2,4,6-tribromophenyl)methyl]carbamate was obtained as a brown semisolid in 66% yield: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta =$ 1.25 (t,  ${}^{3}J = 7.17$  Hz, 3 H, OCH<sub>2</sub>CH<sub>3</sub>), 1.28 [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>], 2.19 (s, 6 H, CH<sub>3</sub>), 4.16 (q,  ${}^{3}J = 7.17$  Hz, 2 H, OCH<sub>2</sub>CH<sub>3</sub>), 5.23 (d,  ${}^{3}J = 8.82$  Hz, 1 H, ArCHAr), 6.39 (d,  ${}^{3}J = 8.82$  Hz, 1 H, NH), 6.96 (s, 2 H, ArH), 7.71 (s, 2 H, ArH) ppm. <sup>13</sup>C NMR (75 MHz,  $CDCl_3$ ):  $\delta = 14.7 (OCH_2CH_3), 21.3 (CH_3), 31.2 [C(CH_3)_3], 34.1$ [C(CH<sub>3</sub>)<sub>3</sub>], 57.9 (OCH<sub>2</sub>CH<sub>3</sub>), 61.2 (ArCHAr), 120.9 (Ar), 125.0 (Ar), 126.9 (Ar), 132.3 (Ar), 136.3 (Ar), 136.8 (Ar), 137.5 (Ar), 150.6 (Ar), 154.9 (C=O) ppm. MS: m/z (%) = 579 (M +6, 2.7), 577 (M +4, 7.8), 575 (M +2, 7.6), 573 (2.8) [M<sup>+</sup>], 496 (82.6), 57 (100). HRMS for C<sub>22</sub>H<sub>26</sub>NO<sub>2</sub>Br<sub>3</sub>: calcd. 572.9512; found 572.9516. To a vigorously stirred mixture of the carbamate (4.3 g, 7.5 mmol) in acetic acid (30 mL) and acetic anhydride (40 mL) at 0 °C was added a 1.0 g portion of sodium nitrite every 20 min for 3 h (total 10.0 g, 149 mmol). The mixture was stirred overnight at room temperature, poured onto ice water(50 mL), and extracted with Et<sub>2</sub>O. The ethereal layer was washed with 5% Na<sub>2</sub>CO<sub>3</sub> solution and water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and the solvents evaporated to give ethyl N-nitroso-N-[(4-tert-butyl-2,6-dimethylphenyl)(2,4,6-tribromophenyl)methyl]carbamate as a brown solid in 95% yield: <sup>1</sup>H NMR  $(300 \text{ MHz}, \text{CDCl}_3)$ :  $\delta = 1.22 \text{ (t, } {}^{3}J = 7.17 \text{ Hz}, 3 \text{ H}, \text{ OCH}_2\text{CH}_3)$ 1.27 [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>], 1.96 (s, 6 H, CH<sub>3</sub>), 4.35 (q,  ${}^{3}J = 7.17$  Hz, 2 H, OCH2CH3), 6.91 (br. s, 3 H, ArCHAr and ArH), 7.69 (s, 2 H, ArH) ppm. Potassium tert-butoxide (1.39 g, 12.4 mmol) was added to a solution of the nitroso compound (3.0 g, 5.0 mmol) in anhydrous THF (50 mL) under an argon atmosphere. The mixture was stirred overnight at room temperature, poured onto water, and extracted with Et2O. The ethereal layer was washed with water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and the solvents evaporated. The reaction mixture was passed through a column (aluminum oxide deactivated with 5% water, n-hexane), and the first fraction was purified by GPC (5 cycles, CHCl<sub>3</sub>) to afford 1a as an orange solid

in 53% yield. M.p. 117.3–118.0 °C dec. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.30 [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>], 2.15 (s, 6 H, CH<sub>3</sub>), 7.08 (s, 2 H, ArH), 7.74 (s, 2 H, ArH) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 21.2 (CH<sub>3</sub>), 31.3 [C(CH<sub>3</sub>)<sub>3</sub>], 34.3 [C(CH<sub>3</sub>)<sub>3</sub>], 63.1 (ArCAr), 121.1 (Ar), 124.5 (Ar), 125.7 (Ar), 126.0 (Ar), 131.6 (Ar), 135.6 (Ar), 137.3 (Ar), 150.9 (Ar) ppm. IR (NaCl):  $\tilde{v}$  = 2054 cm<sup>-1</sup>.

Preparation of (4-tert-Butyl-2,6-dimethylphenyl)(2,6-dibromo-4ethynylphenyl)diazomethane (2a): To a mixture of diazomethane 1a (82.4 mg, 0.16 mmol), bis(triphenylphosphane)palladium dichloride (10 mg, 0.014 mmol), and copper(I) iodide(catalytic amount) in anhydrous triethylamine (1 mL) was added trimethylsilylacetylene (67.8 µL, 0.48 mmol) at room temperature under a nitrogen atmosphere. The mixture was stirred overnight at 40 °C, evaporated, passed through a column (aluminum oxide deactivated with 5% water, n-hexane), and purified by GPC (8 cycles, CHCl<sub>3</sub>). The diazomethane 2a-TMS was obtained as an orange solid in 50% yield. M.p. 48.5–49.5.0 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 0.24$  [s, 9 H, Si(CH<sub>3</sub>)<sub>3</sub>], 1.30 [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>], 2.14 (s, 6 H, CH<sub>3</sub>), 7.07 (s, 2 H. ArH), 7.66 (s. 2 H. ArH) ppm, <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>);  $\delta = -0.2$  [Si(CH<sub>3</sub>)<sub>3</sub>], 21.1 (CH<sub>3</sub>), 31.3 [C(CH<sub>3</sub>)<sub>3</sub>], 34.3 [C(CH<sub>3</sub>)<sub>3</sub>], 63.7 (ArCAr), 97.9 (ArCCTMS), 101.5 (ArCCTMS), 124.3 (Ar), 124.6 (Ar), 124.7 (Ar), 125.9 (Ar), 132.6 (Ar), 136.2 (Ar), 137.4 (Ar), 150.9 (Ar) ppm. IR (NaCl):  $\tilde{v} = 2162$ , 2053 cm<sup>-1</sup>. A mixture of the latter diazomethane (158 mg, 0.30 mmol), tert-butyl alcohol (10 mL), and 10% NaOH solution (4 mL) was stirred overnight at room temperature. The mixture was poured onto water and extracted with Et<sub>2</sub>O. The ethereal layer was washed with water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and the solvents evaporated. The reaction mixture was purified by GPC (3 cycles, CHCl<sub>3</sub>) to afford 2a as a yellow semisolid in 85% yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta =$ 1.30 [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>], 2.15 (s, 6 H, CH<sub>3</sub>), 3.16 (s, 1 H, ArCCH), 7.08 (s, 2 H, ArH), 7.68 (s, 2 H, ArH) ppm. <sup>13</sup>C NMR (75 MHz,  $CDCl_3$ ):  $\delta = 21.1 (CH_3), 31.3 [C(CH_3)_3], 34.3 [C(CH_3)_3], 63.7 (Ar-$ CAr), 80.2 (ArCCH), 80.4 (ArCCH), 123.2, 124.6 (Ar), 125.9 (Ar), 133.1 (Ar), 136.4 (Ar), 137.5 (Ar), 151.0 (Ar) ppm. IR (NaCl):  $\tilde{v} =$ 3300, 2157, 2055 cm<sup>-1</sup>.

Preparation of Tris(diazo) Compound 3a: To a mixture of diazomethane 2a (24.5 mg, 0.053 mmol), 1,3,5-triiodobenzene<sup>[27]</sup> (8.1 mg, 0.018 mmol), bis(triphenylphosphane)palladium dichloride (10 mg, 0.014 mmol), and copper(I) iodide(catalytic amount) was added anhydrous triethylamine (1 mL) at room temperature under a nitrogen atmosphere. The mixture was stirred at room temperature for 2 days, evaporated, passed through a column (aluminum oxide deactivated with 5% water, n-hexane), and purified by GPC (3 cycles, CHCl<sub>3</sub>). Tris(diazo) compound 3a was obtained from the first fraction as an orange semisolid in 50% yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 1.31$  [s, 27 H, C(CH<sub>3</sub>)<sub>3</sub>], 2.18 (s, 18 H, CH<sub>3</sub>), 7.10 (s, 6 H, ArH), 7.62 (s, 3 H, ArH), 7.74 (s, 6 H, ArH) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 21.2$  (CH<sub>3</sub>), 31.3 [C(CH<sub>3</sub>)<sub>3</sub>], 34.4 [C(CH<sub>3</sub>)<sub>3</sub>], 63.8 (ArCAr), 87.8 (ArCCAr), 90.2 (ArCCAr), 123.5 (Ar), 123.7 (Ar), 124.7 (Ar), 124.8 (Ar), 126.0 (Ar), 132.9 (Ar), 134.6 (Ar), 135.9 (Ar), 137.5 (Ar), 151.1 (Ar) ppm. IR (NaCl):  $\tilde{v} = 2048 \text{ cm}^{-1}$ .

**Preparation of Hexakis(diazo) Compound 6a:** To a mixture of diazomethane **2a** (97.0 mg, 0.210 mmol), 2-(3,5-diiodophenyl)-1-(trimethylsilyl)acetylene (4)<sup>[16]</sup> (44.9 mg, 0.105 mmol), bis(triphenylphosphane)palladium dichloride (10 mg, 0.014 mmol), and copper(1) iodide(catalytic amount) was added anhydrous triethylamine (3 mL) at room temperature under a nitrogen atmosphere. The mixture was stirred at room temperature for 2 days. After workup of the reaction, the crude product was purified by GPC (3 cycles, CHCl<sub>3</sub>). The bis(diazo) compound **5a**-TMS was obtained from the first fraction as an orange solid in 86% yield. Dec. 109.4-110.2 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 0.26$  [s, 9 H, Si(CH<sub>3</sub>)<sub>3</sub>], 1.31 [s, 18 H, C(CH<sub>3</sub>)<sub>3</sub>], 2.17 (s, 12 H, CH<sub>3</sub>), 7.09 (s, 4 H, ArH), 7.56-7.58 (m, 3 H, ArH), 7.72 (s, 4 H, ArH) ppm. <sup>13</sup>C NMR  $(75 \text{ MHz}, \text{ CDCl}_3): \delta = -0.2 [Si(CH_3)_3], 21.2 (CH_3), 31.3$ [C(CH<sub>3</sub>)<sub>3</sub>], 34.3 [C(CH<sub>3</sub>)<sub>3</sub>], 63.8 (ArCAr), 87.5 (ArCCAr), 90.4 (ArCCAr), 96.5 (ArCCTMS), 102.7 (ArCCTMS), 123.1 (Ar), 123.8 (Ar), 124.2 (Ar), 124.67 (Ar), 124.73 (Ar), 126.0 (Ar), 132.8 (Ar), 134.2 (Ar), 135.0 (Ar), 135.9 (Ar), 137.5 (Ar), 151.0 (Ar) ppm. IR (NaCl):  $\tilde{v} = 2155$ , 2055 cm<sup>-1</sup>. A mixture of the bis(diazo) compound 5a-TMS (74.6 mg, 0.068 mmol), MeOH/THF (10 mL), and 10% K<sub>2</sub>CO<sub>3</sub> solution (4 mL) was stirred overnight at room temperature. After workup of the reaction, the crude product was purified by GPC (3 cycles, CHCl<sub>3</sub>) to afford the bis(diazo) compound 5a as an orange solid in 64% yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 1.31$  [s, 18 H, C(CH<sub>3</sub>)<sub>3</sub>], 2.17 (s, 12 H, CH<sub>3</sub>), 3.14 (s, 1 H, ArCCH), 7.09 (s, 4 H, ArH), 7.59-7.62 (m, 3 H, ArH), 7.73 (s, 4 H, ArH) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 21.2$  (CH<sub>3</sub>), 31.3 [C(CH<sub>3</sub>)<sub>3</sub>], 34.3 [C(CH<sub>3</sub>)<sub>3</sub>], 63.8 (ArCAr), 78.9 (ArCCH), 81.5 (ArCCH), 87.7 (ArCCAr), 90.2 (ArCCAr), 123.2 (Ar), 123.3 (Ar), 123.7 (Ar), 124.66 (Ar), 124.74 (Ar), 126.0 (Ar), 132.9 (Ar), 134.7 (Ar), 135.1 (Ar), 135.9 (Ar), 137.5 (Ar), 151.0 (Ar) ppm. IR (NaCl):  $\tilde{v} = 2154, 2055 \text{ cm}^{-1}$ . To a mixture of the bis(diazo) compound **5a** (44.4 mg, 0.044 mmol), 1,3,5-triiodobenzene (6.6 mg, 0.015 mmol), bis(triphenylphosphane)palladium dichloride (10 mg, 0.014 mmol), and copper(I) iodide(catalytic amount) was added anhydrous triethylamine (1 mL) at room temperature under a nitrogen atmosphere. The mixture was stirred at room temperature for 2 days. After workup of the reaction, the crude product was purified by GPC (5 cycles, CHCl<sub>3</sub>) to afford the hexakis(diazo) compound 6a as an orange solid in 79% yield. Dec. 128.9-132.0 °C. <sup>1</sup>H NMR  $(300 \text{ MHz}, \text{ CDCl}_3)$ :  $\delta = 1.31 \text{ [s, 54 H, C(CH_3)_3]}, 2.17 \text{ (s, 36 H, })$ CH<sub>3</sub>), 7.10 (s, 12 H, ArH), 7.63 (t,  ${}^{4}J = 1.53$  Hz, 3 H, ArH), 7.65  $(d, {}^{4}J = 1.53 \text{ Hz}, 6 \text{ H}, \text{ ArH}), 7.68 (s, 3 \text{ H}, \text{ ArH}), 7.75 (s, 12 \text{ H}, 7.75 \text{ H})$ ArH) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 21.2$  (CH<sub>3</sub>), 31.3 [C(CH<sub>3</sub>)<sub>3</sub>], 34.3 [C(CH<sub>3</sub>)<sub>3</sub>], 63.8 (ArCAr), 87.8 (ArCCAr), 90.2 (ArCCAr), 123.4 (Ar), 123.7 (Ar), 124.6 (Ar), 124.6 (Ar), 126.0 (Ar), 132.9 (Ar), 134.6 (Ar), 135.9 (Ar), 137.5 (Ar), 151.0 (Ar) ppm. IR (NaCl):  $\tilde{v} = 2213$ , 2054 cm<sup>-1</sup>.

Preparation of Dodecakis(diazo) Compound 8a: To a mixture of the bis(diazo) compound 5a (65.0 mg, 0.064 mmol), 3,5-diiodotrimethylsilylethynylbenzene 4 (13.6 mg, 0.032 mmol), bis(triphenylphosphane)palladium dichloride (10 mg, 0.014 mmol), and copper(I) iodide(catalytic amount) was added anhydrous triethylamine (4 mL) at room temperature under a nitrogen atmosphere. The mixture was stirred at room temperature for 2 days. After workup of the reaction, the crude product was purified by GPC (7 cycles, CHCl<sub>3</sub>). The tetrakis(diazo) compound 7a-TMS was obtained from the first fraction as an orange semisolid in 67% yield. <sup>1</sup>H NMR  $(300 \text{ MHz}, \text{ CDCl}_3)$ :  $\delta = 0.27 \text{ [s, 9 H, Si(CH_3)_3]}, 1.31 \text{ [s, 36 H,}$ C(CH<sub>3</sub>)<sub>3</sub>], 2.17 (s, 24 H, CH<sub>3</sub>), 7.09 (s, 8 H, ArH), 7.64-7.62 (m, 9 H, ArH), 7.74 (s, 8 H, ArH) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = -0.2$  [Si(CH<sub>3</sub>)<sub>3</sub>], 21.3 (CH<sub>3</sub>), 31.5 [C(CH<sub>3</sub>)<sub>3</sub>], 34.5 [C(CH<sub>3</sub>)<sub>3</sub>], 64.0 (ArCAr), 87.9 (ArCCAr), 88.8 (ArCCAr), 89.4 (ArCCAr), 90.5 (ArCCAr), 96.0 (ArCCTMS), 103.1 (ArCCTMS), 123.6 (Ar), 124.4 (Ar), 123.9 (Ar), 124.9 (Ar), 124.9 (Ar), 126.1 (Ar), 133.1 (Ar), 134.4 (Ar), 135.5 (Ar), 136.1 (Ar), 137.7 (Ar), 151.2 (Ar) ppm. IR (NaCl):  $\tilde{v} = 2213$ , 2158, 2056 cm<sup>-1</sup>. A mixture of the tetrakis-(diazo) compound 7a (47.3 mg, 0.022 mmol), tert-butyl alcohol (15 mL), benzene (10 mL), and 10% NaOH solution (5 mL) was stirred overnight at room temperature. After workup of the reaction mixture, the crude product was purified by GPC (2 cycles, CHCl<sub>3</sub>) to afford tetrakis(diazo) compound 7a as an orange solid

in 72% yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>2</sub>):  $\delta = 1.31$  [s, 36 H, C(CH<sub>3</sub>)<sub>3</sub>], 2.17 (s, 24 H, CH<sub>3</sub>), 3.15 (s, 1 H, ArCCH), 7.09 (s, 8 H, ArH), 7.62-7.65 (m, 9 H, ArH), 7.74 (s, 8 H, ArH) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 21.2$  (CH<sub>3</sub>), 31.3 [C(CH<sub>3</sub>)<sub>3</sub>], 34.3 [C(CH<sub>3</sub>)<sub>3</sub>], 63.8 (ArCAr), 78.8 (ArCCH), 81.7 (ArCCH), 87.8 (ArCCAr), 88.8 (ArCCAr), 89.0 (ArCCAr), 90.3 (ArCCAr), 123.5 (Ar), 123.5 (Ar), 123.7 (Ar), 124.7 (Ar), 124.8 (Ar), 126.0 (Ar), 132.9 (Ar), 134.6 (Ar), 135.9 (Ar), 137.5 (Ar), 151.0 (Ar) ppm. IR (NaCl):  $\tilde{v} = 2253$ , 2055 cm<sup>-1</sup>. To a mixture of tetrakis(diazo) compound 7a (20.0 mg, 9.4 µmol), 1,3,5-triiodobenzene (1.4 mg, 3.1 µmol), bis(triphenylphosphane)palladium dichloride (10 mg, 14 µmol), and copper(I) iodide (catalytic amount) was added anhydrous triethylamine (1.5 mL) at room temperature under a nitrogen atmosphere. The mixture was stirred at room temperature for 2 days. After workup of the reaction, the crude product was purified by GPC (5 cycles, CHCl<sub>3</sub>) to afford dodecakis(diazo) compound 8a as an orange solid in 60% yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 1.31$  (s, 108 H, C(CH<sub>3</sub>)<sub>3</sub>], 2.17 (s, 72 H, CH<sub>3</sub>), 7.08 (s, 24 H, ArH), 7.58-7.71 (m, 30 H, ArH), 7.71 (s, 12 H, ArH), 7.73 (s, 12 H, ArH) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 21.2$  (CH<sub>3</sub>), 31.3 [C(CH<sub>3</sub>)<sub>3</sub>], 34.3 [C(CH<sub>3</sub>)<sub>3</sub>], 63.8 (ArCAr), 87.9 (ArCCAr), 88.8 (ArCCAr), 89.0 (ArCCAr), 89.2 (ArCCAr), 90.3 (ArCCAr), 90.3 (ArCCAr), 123.5 (Ar), 123.5 (Ar), 123.7 (Ar), 124.7 (Ar), 124.8 (Ar), 126.0 (Ar), 132.9 (Ar), 134.6 (Ar), 135.9 (Ar), 137.5 (Ar), 151.1 (Ar) ppm. IR (NaCl):  $\tilde{v} = 2052 \text{ cm}^{-1}$ .

Preparation of (4-tert-Butyl-2,6-dimethylphenyl)(2,4,6-tribromophenyl)methanone (1b): A mixture of chromium(IV) oxide (7.9 g, 79 mmol), concentrated sulfuric acid (8 mL), and water (15 mL) was added dropwise over 30 minutes at room temperature to a solution of (4-tert-butyl-2,6-dimethylphenyl)(2,4,6-tribromophenyl)methanol (2.0 g, 4.0 mmol) in acetone (40 mL). The mixture was stirred for 3 h. After adding 2-propanol (6 mL), the solvent was removed by rotary evaporator, and the mixture was extracted with diethyl ether. The organic layer was washed with Na<sub>2</sub>CO<sub>3</sub> and water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and the solvents evaporated to give **1b** as white needles in 71% yield. M.p. 107.5-107.8 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 1.31$  [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>], 2.28 (s, 6 H, CH<sub>3</sub>), 7.05 (s, 2 H, ArH), 7.78 (s, 2 H, ArH) ppm. <sup>13</sup>C NMR  $(75 \text{ MHz}, \text{CDCl}_3): \delta = 22.0 (\text{CH}_3), 31.0 [C(CH_3)_3], 34.6 [C(CH_3)_3],$ 121.8 (Ar), 123.9 (Ar), 126.7 (Ar), 134.3 (Ar), 135.2 (Ar), 138.5 (Ar), 141.8 (Ar), 154.8 (Ar), 195.6 (ArCOAr) ppm. IR (KBr):  $\tilde{v} =$  $1666 \text{ cm}^{-1}$ . MS: m/z (%) = 506 (M +6, 1.1), 504 (M +4, 2.7), 502 (M + 2, 2.8), 500 (1.1)  $[M^+]$ , 423 (100). HRMS for  $C_{19}H_{19}OBr_3$ : calcd. 499.8985; found 499.9058.

Preparation of Tris(ketone) 3b: (4-tert-Butyl-2,6-dimethylphenyl)[2,6-dibromo-4-(trimethylsilylethynyl)phenyl]methanone (2b-TMS) was obtained by the reaction of benzophenone 1b with trimethylsilylacethylene, followed by column chromatography and GPC, in 56% yield as a white solid. M.p. 136.3-136.8 °C. <sup>1</sup>H NMR  $(300 \text{ MHz}, \text{ CDCl}_3)$ :  $\delta = 0.25 \text{ [s, 9 H, Si(CH_3)_3]}, 1.31 \text{ [s, 9 H,}$ C(CH<sub>3</sub>)<sub>3</sub>], 2.28 (s, 6 H, CH<sub>3</sub>), 7.04 (s, 2 H, ArH), 7.65 (s, 2 H, ArH) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = -0.3$  [Si(CH<sub>3</sub>)<sub>3</sub>], 22.0 (CH<sub>3</sub>), 31.0 [C(CH<sub>3</sub>)<sub>3</sub>]), 34.6 [C(CH<sub>3</sub>)<sub>3</sub>], 99.2 (ArCCSi), 101.0 (ArCCSi), 120.9 (Ar), 126.7 (Ar), 126.7 (Ar), 134.4 (Ar), 135.6 (Ar), 138.6 (Ar), 142.6 (Ar), 154.7 (Ar), 195.9 (ArCOAr) ppm. IR (KBr):  $\tilde{v} = 1670 \text{ cm}^{-1}$ . (4-tert-Butyl-2,6-dimethylphenyl)(2,6-dibromo-4-ethynylphenyl)methanone (2b) was obtained by the reaction of 2b-TMS with K<sub>2</sub>CO<sub>3</sub>, followed by GPC, in 98% yield as a white solid. M.p. 103.0–104.0 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 1.30$  [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>], 2.29 (s, 6 H, CH<sub>3</sub>), 3.23 (s, 1 H, ArCCH), 7.05 (s, 2 H, ArH), 7.67 (s, 2 H, ArH) ppm. <sup>13</sup>C NMR  $(75 \text{ MHz}, \text{ CDCl}_3): \delta = 22.0 (\text{CH}_3), 31.0 [C(CH_3)_3]), 34.6$  [C(CH<sub>3</sub>)<sub>3</sub>], 80.0 (ArCCH), 81.0 (ArCCH), 121.0 (Ar), 125.65 (Ar), 126.7 (Ar), 134.3 (Ar), 135.9 (Ar), 138.6 (Ar), 143.2 (Ar), 154.8 (Ar), 195.8 (ArCOAr) ppm. IR (KBr):  $\tilde{v} = 1667 \text{ cm}^{-1}$ . Tris(ketone) **3b** was obtained by the reaction of **2b** with 1,3,5-triiodobenzene, followed by GPC, in 67% yield as a white solid. M.p. 136.3–136.8 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 1.31$  [s, 27 H, C(CH<sub>3</sub>)<sub>3</sub>], 2.31 (s, 18 H, CH<sub>3</sub>), 7.06 (s, 6 H, ArH), 7.67 (s, 3 H, ArH), 7.73 (s, 6 H, ArH) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 22.0$  (CH<sub>3</sub>), 31.0 [C(CH<sub>3</sub>)<sub>3</sub>]), 34.6 [C(CH<sub>3</sub>)<sub>3</sub>], 87.5 (ArCCAr), 90.7 (ArCCAr), 121.1 (Ar), 123.3 (Ar), 126.0 (Ar), 126.7 (Ar), 134.3 (Ar), 135.0 (Ar), 135.3 (Ar), 138.5 (Ar), 142.8 (Ar), 154.8 (Ar), 195.8 (ArCOAr) ppm. IR (KBr):  $\tilde{v} = 1668 \text{ cm}^{-1}$ . HRMS(ESI) for C<sub>69</sub>H<sub>60</sub>Br<sub>6</sub>O<sub>3</sub>: calcd. 1409.9643; found 1409.9633.

Preparation of Hexakis(ketone) 6b: Trimethylsilylethynyl-bis(ketone) 5b-TMS was obtained by the reaction of ethynyl-benzophenone 2b with 3,5-diiodotrimethylsilylethynylbenzene (4), followed by GPC, in 88% yield as a brown solid. M.p. 138 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 0.26$  (s, 9 H), 1.31 [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>], 2.31 (s, 6 H, CH<sub>3</sub>), 7.06 (s, 4 H, ArH), 7.60 (t,  ${}^{4}J = 1.47$  Hz, 1 H, ArH), 7.62 (d,  ${}^{4}J = 1.47$  Hz, 2 H, ArH), 7.71 (s, 4 H, ArH) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = -0.2$  [Si(CH<sub>3</sub>)<sub>3</sub>], 22.0 (CH<sub>3</sub>), 31.0 [C(CH<sub>3</sub>)<sub>3</sub>]), 34.6 [C(CH<sub>3</sub>)<sub>3</sub>], 87.1 (ArCCTMS), 91.1 (ArCCTMS), 96.8 (ArCCAr), 102.5 (ArCCAr), 121.1 (Ar), 122.9 (Ar), 124.4 (Ar), 126.2 (Ar), 126.7 (Ar), 126.8 (Ar), 134.3 (Ar), 135.3 (Ar), 135.5 (Ar), 138.6 (Ar), 142.8 (Ar), 154.8 (Ar), 195.9 (ArCOAr) ppm. IR (KBr):  $\tilde{v} = 1668 \text{ cm}^{-1}$ . MS (MALDI-TOF) for C<sub>53</sub>H<sub>50</sub>Br<sub>4</sub>O<sub>2</sub>Si: calcd. 1066.027; found 1066.146. Ethynyl-bis(ketone) **5b** was obtained by the reaction of the ketone **5b**-TMS with K<sub>2</sub>CO<sub>3</sub>, followed by GPC, in 66% yield as a brown solid. M.p. 92.3-94.0 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 1.31$  [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>], 2.31 (s, 6 H, CH<sub>3</sub>), 3.16 (s, 1 H, ArCCH), 7.06 (s, 4 H, ArH), 7.63 (d,  ${}^{4}J$  = 1.47 Hz, 2 H, ArH), 7.64 (t,  ${}^{4}J$  = 1.47 Hz, 1 H, ArH), 7.72 (s, 4 H, ArH) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 22.0 (CH_3), 31.0 [C(CH_3)_3]), 34.6 [C(CH_3)_3], 79.2 (ArCCH),$ 81.4 (ArCCH), 87.3 (ArCCAr), 90.9 (ArCCAr), 121.1 (Ar), 123.1 (Ar), 123.4 (Ar), 126.1 (Ar), 126.7 (Ar), 134.3 (Ar), 134.8 (Ar), 135.4 (Ar), 135.4 (Ar), 138.6 (Ar), 142.9 (Ar), 154.8 (Ar), 195.8 (ArCOAr) ppm. IR (KBr):  $\tilde{\nu} = 1667 \text{ cm}^{-1}$ . Hexakis(ketone) **6b** was obtained by the reaction of the ketone 5b with 1,3,5-triiodobenzene, followed by GPC, in 71% yield as a brown solid. M.p. 107.5 - 107.8 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 1.31$  [s, 54 H,  $C(CH_3)_3$ , 2.31 (s, 36 H, CH<sub>3</sub>), 7.06 (s, 12 H), 7.67 (t,  ${}^4J = 1.47$  Hz, 3 H, ArH), 7.69 (d,  ${}^{4}J$  = 1.47 Hz, 6 H, ArH), 7.69 (s, 3 H, ArH), 7.73 (s, 12 H, ArH) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 22.0 (CH<sub>3</sub>), 31.0 [C(CH<sub>3</sub>)<sub>3</sub>]), 34.6 [C(CH<sub>3</sub>)<sub>3</sub>], 87.1 (ArCCAr), 88.7 (ArCCAr), 89.2 (ArCCAr), 90.9 (ArCCAr), 121.1 (Ar), 123.2 (Ar), 123.7 (Ar), 123.9 (Ar), 126.1 (Ar), 126.7 (Ar), 126.9 (Ar), 134.3 (Ar), 134.7 (Ar), 135.4 (Ar), 138.6 (Ar), 142.9 (Ar), 154.8 (Ar), 195.8 (ArCOAr) ppm. IR (KBr):  $\tilde{v} = 1668 \text{cm}^{-1}$ . HRMS (FAB) for C<sub>156</sub>H<sub>126</sub>Br<sub>12</sub>O<sub>6</sub>: calcd. 3041.9755; found 3041.9755.

**Preparation of Dodecakis(ketone) Compound 8b:** To a mixture of ethynyl-bis(ketone) **5b** (90 mg, 90.5 mmol), 3,5-diiodotrimethyl-silylethynylbenzene **4** (19 mg, 45.2 µmol), bis(triphenylphosphane)-palladium dichloride (4.5 mg, 6.3 µmol), and copper(I) iodide (catalytic amount) was added anhydrous triethylamine (3 mL) at 35 °C under an argon atmosphere. The mixture was stirred overnight at 35 °C. After workup of the reaction mixture, the crude product was purified by GPC (7 cycles, CHCl<sub>3</sub>) to afford the tetrakisketone compound **7b**-TMS as a brown solid in 46% yield. M.p. 158.7–159.1 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 0.26$  [s, 9 H, Si(CH<sub>3</sub>)<sub>3</sub>], 1.31 [s, 36 H, C(CH<sub>3</sub>)<sub>3</sub>], 2.31 (s, 24 H, CH<sub>3</sub>), 7.06 (s, 8 H, ArH), 7.64–7.67 (m, 9 H, ArH), 7.74 (s, 8 H, ArH) ppm. <sup>13</sup>C

NMR(75 MHz, CDCl<sub>3</sub>):  $\delta = -0.2$  [Si(CH<sub>3</sub>)<sub>3</sub>], 22.0 (CH<sub>3</sub>), 31.0 [C(CH<sub>3</sub>)<sub>3</sub>]), 34.6 [C(CH<sub>3</sub>)<sub>3</sub>], 87.4 (ArCCTMS), 87.6 (ArCCTMS), 88.4 (ArCCAr), 89.4 (ArCCAr), 90.6 (ArCCAr), 91.0 (ArCCAr), 121.1 (Ar), 123.2 (Ar), 123.3 (Ar), 123.4 (Ar), 124.0 (Ar), (Ar), 124.3 (Ar), 126.0 (Ar), 126.1 (Ar), 126.7 (Ar), 134.3 (Ar), 134.6 (Ar), 135.0 (Ar), 135.4 (Ar), 138.6 (Ar), 142.9 (Ar), 154.8 (Ar), 195.8 (ArCOAr) ppm. IR (NaCl):  $\tilde{v} = 2212$ , 1668 cm<sup>-1</sup>. MS (MALDI-TOF) for  $C_{111}H_{94}Br_8O_4Si$ : calcd. 2159.035; found 2159.425. A mixture of 7b-TMS (73.1 mg, 33.9 µmol), tert-butyl alcohol (20 mL), benzene (7 mL), and 5% NaOH aqueous solution (10 mL) was stirred overnight at 35 °C. After workup of the reaction, the crude product was purified by GPC (2 cycles, CHCl<sub>3</sub>) to afford tetrakisketone compound 7b as an brown solid in 51% yield. M.p. 107.4–107.6 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 1.31$  (s, 18 H, C(CH<sub>3</sub>)<sub>3</sub>], 2.31 (s,12 H, CH<sub>3</sub>), 3.16 (s,1 H, ArCCH), 7.06 (s, 4 H, ArH), 7.64–7.67 (m, 9 H, ArH), 7.75 (s, 4 H, ArH) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 22.0$  (CH<sub>3</sub>), 31.0 [C(CH<sub>3</sub>)<sub>3</sub>]), 34.6 [C(CH<sub>3</sub>)<sub>3</sub>], 78.9 (ArCCH), 81.6 (ArCCH), 87.4 (ArCCAr), 89.2 (ArCCAr), 90.6 (ArCCAr), 90.9 (ArCCAr), 121.1 (Ar), 123.2 (Ar), 123.3 (Ar), 123.4 (Ar), 123.5 (Ar), 123.9 (Ar), 126.1 (Ar), 126.7 (Ar), 134.3 (Ar), 134.7 (Ar), 135.0 (Ar), 135.2 (Ar), 135.4 (Ar), 138.6 (Ar), 142.9 (Ar), 154.8 (Ar), 195.8 (ArCOAr) ppm. IR (NaCl):  $\tilde{v} = 2213$ , 1668 cm<sup>-1</sup>. To a mixture of tetrakisketone compound **7b** (36.0 mg, 17.4 µmol), 1,3,5-triiodobenzene (2.6 mg, 5.8 µmol), bis(triphenylphosphane)palladium dichloride (1.0 mg, 1 µmol), and copper(I) iodide(catalytic amount) was added anhydrous triethylamine (2 mL) at 35 °C under an argon atmosphere. The mixture was stirred overnight at 35 °C. After workup of the reaction, the crude product was purified by GPC (7 cycles, CHCl<sub>3</sub>) to afford 8b as a brown solid in 16% yield. M.p. 187.6-189.0 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 1.31$  (s, 108 H, C(CH<sub>3</sub>)<sub>3</sub>], 2.17 (s, 72 H, CH<sub>3</sub>), 7.08 (s, 24 H, ArH), 7.58–7.71 (m, 30 H, ArH), 7.71 (s, 12 H, ArH), 7.73 (s, 12 H, ArH) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 22.0$  (CH<sub>3</sub>), 31.0 [C(CH<sub>3</sub>)<sub>3</sub>]), 34.6 [C(CH<sub>3</sub>)<sub>3</sub>], 87.4 (ArCCAr), 88.9 (ArCCAr), 89.2 (ArCCAr), 90.88 (ArCCAr), 90.94 (ArCCAr), 93.9 (ArCCAr), 121.1 (Ar), 123.2 (Ar), 123.8 (Ar), 126.1 (Ar), 126.2 (Ar), 126.7 (Ar), 126.9 (Ar), 134.3 (Ar), 134.7 (Ar), 134.8 (Ar), 135.0 (Ar), 135.3 (Ar), 136.1(Ar), 136.6 (Ar), 138.6 (Ar), 139.0 (Ar), 142.9 (Ar), 154.8 (Ar), 195.8 (ArCOAr) ppm. IR (NaCl):  $\tilde{v} = 2213$ , 1668 cm<sup>-1</sup>.

**EPR Measurements:** The diazo compound was dissolved in 2-methyltetrahydrofuran ( $10^{-3}$  M) and the solution was degassed in a quartz cell by three freeze-degas-thaw cycles. The sample was cooled in an optical transmission EPR cavity usually at 77 K and irradiated with a Wacom 500 W Xe lamp using a Pyrex filter. EPR spectra were measured on a JEOL JES TE 200 spectrometer (Xband microwave unit, 100 kHz field modulation). The signal positions were read with the use of a gaussmeter. A JEOL liquid helium transfer system was attached for the low-temperature measurement. The temperature was controlled by a 9650 Microprocessor-based Digital Temperature Indicator/Controller, and the precision of the measurements is within ±0.1 K and the control ability within ±0.2 K. Errors in the measurements of component amplitudes did not exceed 5%, and the accuracy of the resonance fields determination was within ±0.5 mT.

**Low-Temperature UV/Vis Spectra:** Low-temperature spectra at 77 K were obtained by using an Oxford variable-temperature liquid-nitrogen cryostat (DN, 1704) equipped with a quartz outer window and a sapphire inner window. The sample was dissolved in dry 2-MTHF, placed in a long-necked quartz cuvette of 1-mm path length, and degassed thoroughly by repeated freeze-degas-thaw cycles at a pressure near  $10^{-5}$  Torr. The cuvette was flame-sealed,

under reduced pressure, placed in the cryostat, and cooled to 77 K. The sample was irradiated for several minutes in the spectrometer with a Halos 500-W high-pressure mercury lamp using a Pyrex filter, and the spectral changes were recorded at appropriate time intervals. The spectral changes upon thawing were also monitored by carefully controlling the matrix temperature with an Oxford Instrument Intelligent Temperature Controller (ITC, 4).

SQUID Measurements: Magnetic susceptibility data were obtained on a Quantum Design MPMS-2A Superconducting Quantum Interference Device (SQUID) magnetometer/susceptometer. Irradiation with light from an argon ion laser (488 nm, Omnichrome 543-150BS) through a flexible optical fiber which passes through the inside of the SQUID sample holder was performed inside the sample room of the SQUID apparatus at 5-10 K. One end of the optical fiber was located 40 mm above the sample cell (capsule), and the other was attached to a coupler for the laser. The bottom part of the capsule (6 mm  $\times$  10 mm) without a cap was used as a sample cell. A sample of the solution (60  $\mu$ L, 0.125–0.5 mM) in 2-MTHF was placed in the cell which was held by a straw. Irradiation was continued until there was no further change in the magnetization monitored at 5 K in a constant field of 5 kOe. The magnetization before and after irradiation,  $M_{\rm b}$  and  $M_{\rm a}$ , was measured at 5 K in a field range 0-50 kOe. The plots of the magnetization  $[M = F(M_{\rm a} - M_{\rm b}); F$  is the photolysis factor for diazo compounds] versus the magnetic field were analyzed in terms of the Burillouin function.

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