138 Bull. Chem. Soc. Jpn. Vol. 80, No. 1, 138–157 (2007)

Accounts

From Persistent Triplet Carbenes to Persistent High-Spin Polycarbenes

Tetsuji Itoh,[1] Katsuyuki Hirai,*[2] and Hideo Tomioka*[1]

[1]Chemistry Department for Materials, Faculty of Engineering, Mie University, Tsu, Mie 514-8507

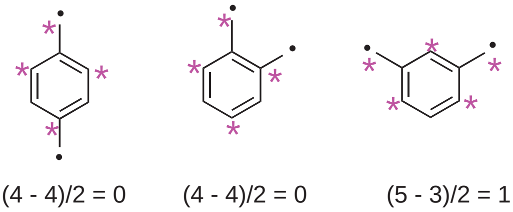
[2]Instrumental Analysis Facilities, Life Science Research Center, Mie University, Tsu, Mie 514-8507

Received February 28, 2006; E-mail: hirai@chem.mie-u.ac.jp

Triplet carbenes are regarded as one of the most effective spin sources for organic ferromagnetic materials since the magnitude of the exchange coupling between the neighboring centers is large. However, those systems have two disadvantages that prevent their use as practical magnetic materials. First, a triplet carbene unit is highly unstable and lacks the stability for practical applications under ambient conditions. Second, diazo groups, which are precursors for triplet carbenes, are generally labile and, hence, cannot be used as building blocks to prepare a more complicated poly(diazo) compound. After great efforts to stabilize the triplet carbenes, we have succeeded in preparing fairly stable triplet carbenes that survive for days. We found that a diazo precursor for a persistent triplet carbene was also persistent and, hence, can be further modified into a more complicated diazo compound that can generate persistent high-spin polycarbenes. In this account, we would like to summarize our efforts along this line. We employed the following three approaches to prepare poly(diazo) compounds; (1) synthesis of dendritic molecules having peripheral diazo groups starting from diazo compounds, (2) preparation of a poly(phenylacetylene) with a diazo unit using Rh-complex-catalyzed polymerization of diazo compounds with *p*-ethynyl substituents, and (3) preparation of a polymer chain as a result of complexation of the pyridine ligand on diazo compounds with coordinatively unsaturated metal ions. We also characterized the magnetic properties of photoproducts obtained by photolysis of those poly(diazo) compounds. Although spin-states observed for those photoproducts were not so high, the results suggest that our approach using persistent triplet carbenes will eventually lead us to a persistent high-spin polycarbenes by taking advantage of the stability of our diazo compounds.

An increasing amount of interest is being paid to molecular magnetism, in which spins of unpaired electrons in π-orbitals of light atoms such as carbon, nitrogen, and oxygen are mainly responsible for the magnetic properties. Many attempts have been made to prepare organic ferromagnetic materials.[1,2] There are two major structural determinants for constructing high-spin organic molecules. The first one is based on a valence bond model, which assumes that electrons are perfectly correlated. Thus, the ground state of any molecule is determined by which set of possible distribution of α- and β-electron spins allows the formation of the maximum number of bonds.[4] This can be simply expressed by Eq. 1, known as Ovchinnikov equation,[3] where the atoms can be divided into two sets, traditionally called starred and unstarred and n^* and n are the numbers of the starred and unstarred atoms. If the numbers of starred and unstarred atoms are equal, the number of α- and β-spin electrons will also be the same, and the ground state will be a singlet. However, if there are more starred atoms than unstarred atoms, the number of α-spin electrons will exceed the number of β-spin electrons by n^* minus n, and hence the spin quantum number will be $(n^* - n)/2$.

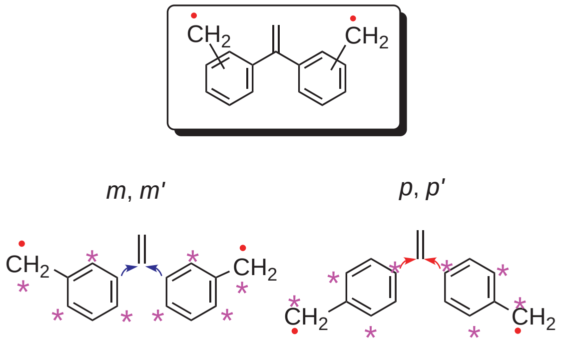
$$S = (n^* - n)/2. \tag{1}$$



Scheme 1. Ground state multiplicity of phenylenebis(methylene)s according to Ovchinnikov equation.

If one applies this equation to predict the ground state multiplicity of phenylenebis(methylene)s isomers, $S = 0$, which is a singlet, is predicted for ortho and para isomers, while $S = 1$, which is a triplet, is predicted for meta isomer. This is exactly what has been observed (Scheme 1).[1a,3]

The second determinant is based on Hückel theory, which focuses only on maximizing the buildup of electron density in the regions where the atomic orbitals on the atoms overlap most strongly.[5,6] If one assumes that diradicals are formed by connecting two monoradicals, there are two possibilities. When one or both of the points of union bears a finite nonbonding molecular orbital (NBMO) coefficient, the exchange



Scheme 2. The connectivity in *m*,*m*′- and *p*,*p*′-vinylidenebis(benzyl)s.

interaction is not zero. This is called non-disjoint. On the other hand, when they are formed by union at the points with no NBMO coefficient, the exchange interaction approaches zero. This is called disjoint.

For instance, for both *m*,*m*′- and *p*,*p*′-vinylidenebis(benzyl), Ovchinnikov rule predicts $S = 1$ by counting the numbers of starred and unstarred carbon atoms. But in *m*,*m*′-isomer, each benzyl radical unit is connected on vinylidene part at the carbon where NBMO coefficients are zero, which is doubly disjoint. Therefore, $S = 0$ is predicted. Experimentally, a triplet ground state has not been observed for this system.[7] For the *p*,*p*′-isomer, each benzyl radical unit is connected at the carbon which has NBMO coefficients, which is non-disjoint. Thus, $S = 1$ is predicted. This has also been verified experimentally.[7] In other words, when two spin systems are connected to a bridging π linker so that they are able to interact ferromagnetically, they should be connected at an atom that has NBMO coefficients (Scheme 2).

Based on these determinants, many attempts have been made to prepare organic ferromagnetic materials. The spin sources used for such studies are mostly thermodynamically stable radicals such as phenoxyls,[8] triphenylmethyls,[9] and aminoxyls.[10] This is obviously due to their ease of preparation and use. However, since the spin state of those radicals is 1/2, they have potential problems. For instance, exchange coupling between neighboring aminoxyls is weak, and contamination of the lower-spin states in the polyradicals cannot be avoided.

Triplet carbenes are regarded as a more attractive spin source since they have two nonbonding electrons on one carbon atom with $S = 1$, and hence, one can generate higher spin states by using the same number of the units with radicals. In addition, the magnitude of the exchange coupling between the neighboring centers is large.[11,12] Moreover, since carbenes are easily generated by photolysis of precursor diazo compounds, one can generate high-spin polycarbenes by photolysis of diamagnetic diazo compounds even at low temperature in rigid matrix.

Actually, Iwamura and co-workers have prepared a "starburst-"type nonakis(diazo) compound and have demonstrated that nine diazo groups are photolyzed at low temperature to give a nonadecet ground state ($S = 9$).[12]

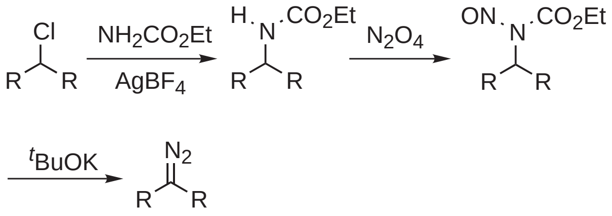
However, those systems have two disadvantages that prevent them from being practical magnetic materials. First, a triplet carbene unit is highly unstable and lacks the stability for practical applications under ambient conditions.[13,14] For instance, triplet diphenylcarbene has a lifetime of 1 micro second in solution at room temperature, while triphenymethyl radical is known to be stable.[14]

In order to overcome these difficulties, we have tried to stabilize and hopefully isolate the triplet carbene and succeeded in preparing fairly stable ones.[15] For instance, triplet diphenylcarbene is stabilized by introducing a bulky but unreactive group at the ortho positions. Thus, triplet diphenylcarbene protected by bromine and trifluoromethyl groups is shown to survive a day on solution at room temperature.[16] Moreover, bis(9-anthryl)carbene which is stabilized not only thermodynamically as a result of extensive delocalization of unpaired electrons onto anthryl rings but also kinetically by four peri hydrogens can be stabilized by introducing a substituent at the position 10; bis[10-(4-*t*-butyl-2,6-dimethylphenyl)-9-anthryl]carbene is shown to survive more than one week in solution at room temperature.[17] Now, we have a fairly stable triplet carbene, the next step is to explore ways to connect them in ferromagnetic fashion to prepare a high-spin polycarbene.

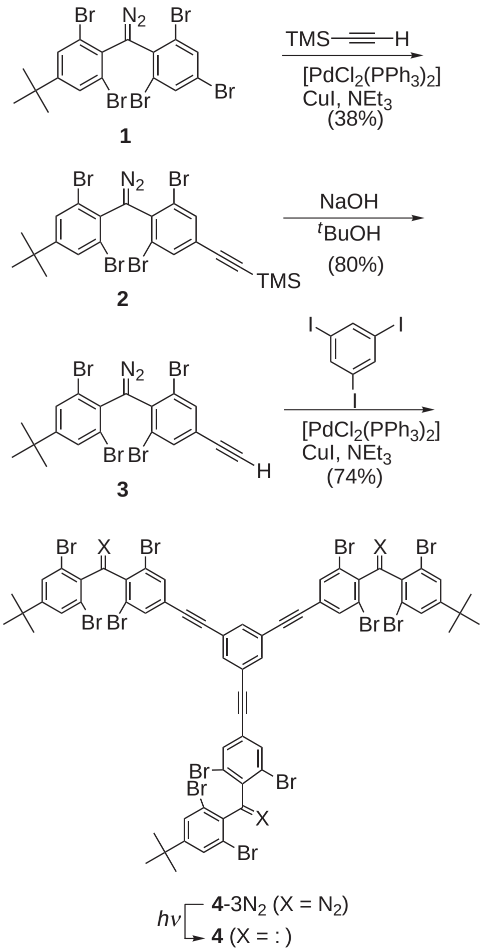
The second disadvantage is that diazo groups are also generally labile not only to heat and light but also to acid and metals which is often employed to modify the compound and, hence, cannot be used as a building block to prepare a more complicated poly(diazo) compound.[18] The diazo functional groups are therefore usually introduced at the last step of synthesis. For instance, Iwamura and co-workers prepared poly(diazo) compound from polyketone which is poly-hydrazonated followed by poly-oxidation.[12] This is very elegant method to prepare poly(diazo) compounds, but this method is applicable only to prepare poly(diazo) compound consisting of simple diphenyldiazomethane unit.

Preparation of the precursor diazomethanes for sterically hindered carbene is not that simple and traditional hydrazonation followed by the oxidation procedures does not work. The synthetic pathway to prepare sterically congested diphenyldiazomethane is summarized in Scheme 3.[18,19] Many steps are required to reach to the desired diazo compound, which suggests that it is impossible to prepare sterically congested poly(diazomethane)s by extending the method.

A solution to a very difficult problem has always been due to a naïve attempt by a student. One of students tried to couple an acetylene unit to polybrominated diphenyldiazomethane (**1**) by using Pd and Cu catalysts, which is known as the Sonogashira coupling reaction (Scheme 4).[20] It is well-known that these metals are good catalysts for decomposing diazo groups.[18,21] Thus, one might expect that decomposition of the diazo functional groups may occur. However, the cross-coupling reaction proceeded with the diazo group intact, and



Scheme 3.



Scheme 4.

the student was able to isolate the desired ethynylated diphenyldiazomethane (**2**) in a fairly good yield. This is initially surprising but not so surprising when one examines the X-ray crystal structure of bis(2,4,6-tribromophenyl)diazomethane,[22] in which the four bromine groups at the ortho positions that were introduced to block the carbene center and to protect the diazo carbon from external reagents. Therefore, only the para carbon is exposed to be attacked by the reagents. In other words, the diazomethane prepared to generate a stable carbene is also stable and, hence, can be used as a building block to construct more complicated poly(diazo) compounds in order to generate high-spin polycarbenes. Encouraged by this finding, we decided to prepare poly(diazo) compounds and to characterize spin states of polycarbenes generated by photolysis of those poly(diazo) compounds.

We employed following three approaches to prepare poly(diazo) compounds; (1) synthesis of dendritic molecules having peripheral diazo groups starting from monomeric diaryldiazomethanes, (2) preparation of a poly(phenylacetylene) bearing diazo unit using the Rh-complex-catalyzed polymerization of diaryldiazomethanes bearing *p*-ethynyl substituents, and (3) preparation of polymer chain as a result of complexation of the ligand pyridine introduced on monomeric diaryldiazomethanes with coordinatively unsaturated metal ions. Here, we would like to summarize our observations in this order.

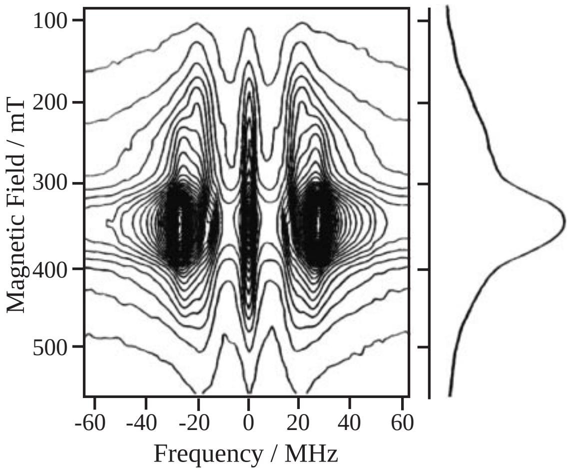


Fig. 1. Contour plot of field-swept 2D nutation spectra of **4** observed at 5 K in a 2-methyltetrahydrofuran (2-MTHF) glass. On the right, an electron spin-echo detected fine-structure ESR spectrum is given.

1. Dendrimer Approach

1.1 Dendrimer by Connecting Diphenyldiazomethanes through Ethynyl Group on Benzene Unit.

One way to prepare poly(diaryldiazomethane)s is to connect diaryldiazomethane units in a dendrimer arrangement. Since we were able to introduce an ethynyl handle on diaryldiazomethanes by Sonogashira coupling reaction, we first prepared a dendritic diazo compound by extending this method.

Deprotection[23] of the trimethylsilyl group of **2** gave **3**. Subsequent coupling with 1,3,5-triiodobenzene took place smoothly to produce tris(diazo) compound **4**–3N$_2$ (Scheme 4),[24] where three carbene precursor units have been introduced so as to generate tris(carbene), connected in a ferromagnetic fashion based on the Ovchinnikov equation.[4] Photolysis ($\lambda > 300$ nm) of **4**–3N$_2$ in a 2-methyltetrahydrofuran (2-MTHF) glass at 5 K gave a fine-structure ESR spectrum which was different from that observed by the photolysis of bis(2,4,6-tribromophenyl)diazomethane.[15a] However, it is obvious why conventional continuous-wave (CW) ESR spectroscopy for randomly oriented organic high-spin species fails to give evidence for the spin state of the tris(carbene).

To identify the spin multiplicity of the tris(carbene) **4** unequivocally, field-swept two-dimensional electron spin transient resonance (2D-ESTN) spectroscopy for nonoriented high-spin sysytems[25,26] was used. This technique is based on a pulsed FT-ESR spectroscopic method[25–28] and can be used to determine the electronic and environmental structures of high-spin species even in amorphous materials, which is not possible using CW ESR.[25,26] After photolysis of **4**–3N$_2$ under the same conditions as for CW ESR, a contour plot of field-swept 2D-ESTN spectra of **4** was obtained (Fig. 1). Three dominant peaks of the nutation spectra in the range 200–350 mT were observed at 22.0, 27.5, and 29.5 MHz. The observed ratio of 22.0:27.5:29.5 agrees with the theoretical value. These theoretical frequency values correspond to the allowed ESR transitions for septet states, meaning that the observed fine-structure is due to a spin-septet state. Between 2.6 and 90 K, no other nutation peaks attributable to lower spin states ($S > 1$) were observed, showing the septet state to be the ground state with the excited low-spin states located above $300\,\mathrm{cm}^{-1}$.

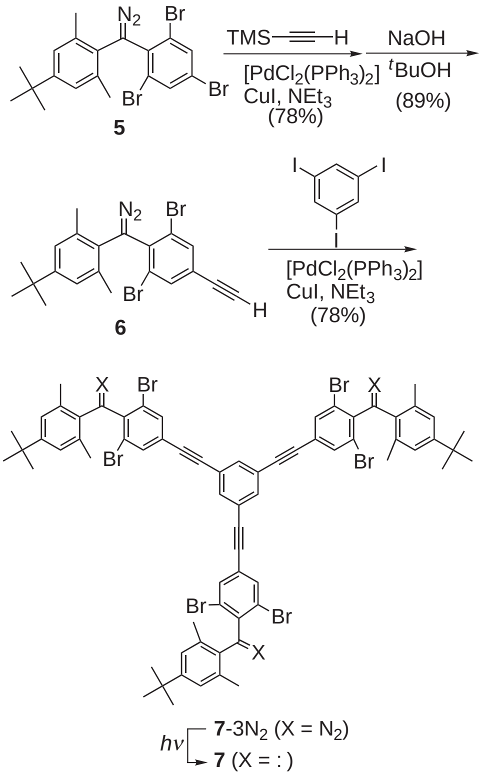
Nutation peaks arising from by-products in a doublet state were not detected, showing the remarkable chemical stability of the tris(carbene) **4**. Also, **4** was shown to be thermally stable during the annealing process. A significant change in the ESR signal shape was observed when the matrix temperature was raised above 140 K and kept for 15 min. New fine-structure signals were irreversible with temperature, and they were characteristic of the small fine-structure constants. They were also determined to originate from a septet ground state by 2D-ESTN spectroscopy. This is in a sharp contrast with that observed for septet state 1,3,5-tris(phenylmethylene)benzene, which has been shown to be persistent only up to 85[29] and 50 K[12c] in rigid glasses.

Encouraged by the finding, we prepared a high-order dendritic diazo compound. Methods for synthesis of phenylacetylene dendritic macromolecules have been developed.[30] The divergent method is hampered by the poor solubility of the growing macromolecules,[30,31] and it also requires rather harsh conditions for the synthetic cycle to be completed. The convergent method has several advantages over the divergent method. Above all, the synthetic cycle can be completed under very mild conditions.[30,31] This is especially important for constructing a dendrimer carrying a chemically sensitive functional group such as a diazo group.

(4-*t*-Butyl-2,6-dimethylphenyl)(2,4,6-tribromophenyl)diazomethane (**5**) was selected as a starting diazo precursor for the following reasons. The alkyl groups, i.e., methyl and *t*-butyl groups, on one side of phenyl ring in **5** are expected to both protect the carbenic center and also improve solubility, which will become a serious problem at a higher generation.

The treatment of **5** with trimethylsilylacetylene in the presence of palladium catalysts gave (4-*t*-butyl-2,6-dimethylphenyl)[2,6-dibromo-4-(trimethylsilylethynyl)phenyl]diazomethane. Deprotection[23] of the trimethylsilyl group in the diazomethane gave (4-*t*-butyl-2,6-dimethylphenyl)(2,6-dibromo-4-ethynylphenyl)diazomethane (**6**). Before converting **6** into the zero-generation monodendron by reacting it with an appropriate difunctional monomer, we coupled it with 1,3,5-triiodobenzene. The coupling reaction proceeded smoothly under mild conditions to form 1,3,5-tris{2-[4-(α-diazo-4-*t*-butyl-2,6-dimethylbenzyl)-3,5-dibromophenyl]ethynyl}benzene (**7**–$3N_2$) (Scheme 5).[32]

In order to obtain evidence concerning the spin states of the photoproducts from **7**–$3N_2$, the magnetic susceptibility of the photoproduct was measured. As noted previously, it is more difficult to obtain unequivocal evidence of the spin states for randomly oriented organic species from the conventional continuous-wave (CW) ESR spectroscopy as the spin states become higher. Bulk magnetization (M), which is an average (thermal) magnetic moment of the sample, can be determined. Magnetometers based on superconducting quantum interference devices (SQUIDs) have gained popularity because of their sensitivity. M is typically measured as a function of temperature (T) and applied static magnetic field (H). Static magnetic susceptibility χ is calculated as $\chi = M/H$.



Scheme 5.

Thus, the 2-MTHF solution of **7**–$3N_2$ (0.5 mM) was placed inside the sample compartment of the SQUID magnet/susceptometer and irradiation at 5–10 K with a light ($\lambda = 488$ nm) from an argon ion laser through an optical fiber was performed. The development of magnetization at 5 K in a constant field of 5 kOe with irradiation time for **7**–$3N_2$ was measured in situ and is shown in Fig. 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, Mb and Ma, respectively, was measured at 2 and 5 K in a field range of 0–50 kOe. The paramagnetic contribution was obtained by subtracting the corresponding values obtained before and after irradiation (Fig. 2B). The effect of any paramagnetic impurities can be cancelled by this treatment. The plots of the magnetization ($M = M\mathrm{a} - M\mathrm{b}$) versus the temperature-normalized magnetic field (H/T) were analyzed in terms of the Brillouin function as follows:[1c,12,33]

$$M = M\mathrm{a} - M\mathrm{b} = FNgJ\mu_\mathrm{B}B(x), \tag{2}$$

where $B(x) = [(2J+1)/2J]\coth\{[(2J+1)/2J]x\} - [1/2J]\coth(x/2J)$ and $x = Jg\mu_\mathrm{B}H/k_\mathrm{B}T$. F is the photolysis factor of diazo compounds, N is the number of molecules, J is the quantum number for the total angular momentum, μ_B is the Bohr magneton, g is the Landé g-factor, and k_B is the Boltzmann constant. Since these carbenes are made 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 Fig. 3 together with theoretical curves with $S = 2$ and 3. The observed data (M/Ms vs H/T) for the photoproduct of the tris(diazo) compound (**7**–$3N_2$) closely traced the theoretical curve with $S = 3$. The data were fitted with Eq. 2 with $S = 2.42$ and

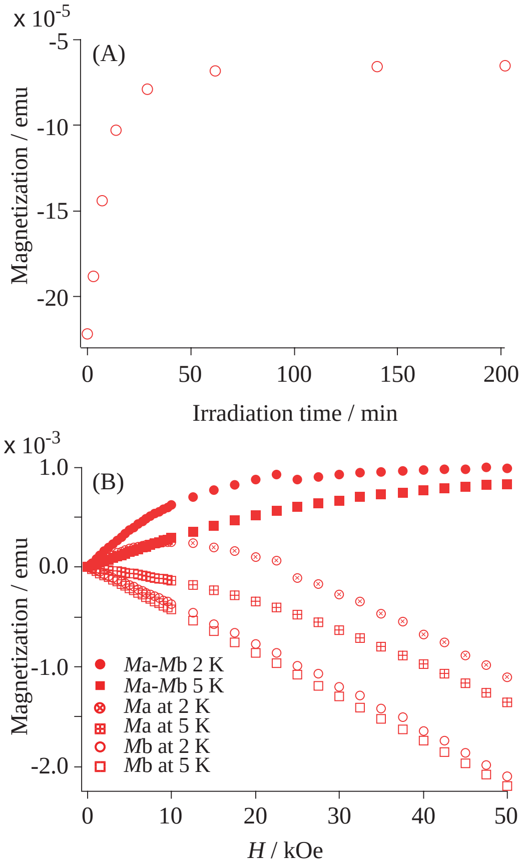


Fig. 2. (A) Plot of magnetization (M) as a function of irradiation time observed in the photolysis of tris(diazo) compound **7**–3N$_2$ in 0.5 mM 2-MTHF matrix measured at 5.0 K and 5 kOe. (B) Field dependence of the magnetization of the photoproduct from tris(diazo) compound **7**–3N$_2$ in 0.5 mM 2-MTHF matrix measured at 2.0 and 5.0 K. Mb and Ma refer to the magnetization value before and after irradiation, respectively, and $M = M\mathrm{a} - M\mathrm{b}$.

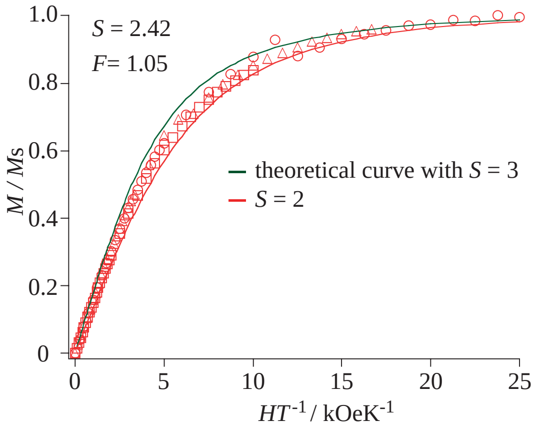


Fig. 3. Plot of magnetization (M) normalized by saturation magnetization (Ms) vs temperature-normalized magnetic field (H/T) obtained upon photolysis of tris(diazo) compound **7**–3N$_2$ measured at 2.0 and 5.0 K. Theoretical curves with $S = 2$ and 3 are also indicated.

$F = 1.05$. The value is somewhat smaller than the theoretically predicted one, which is 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.

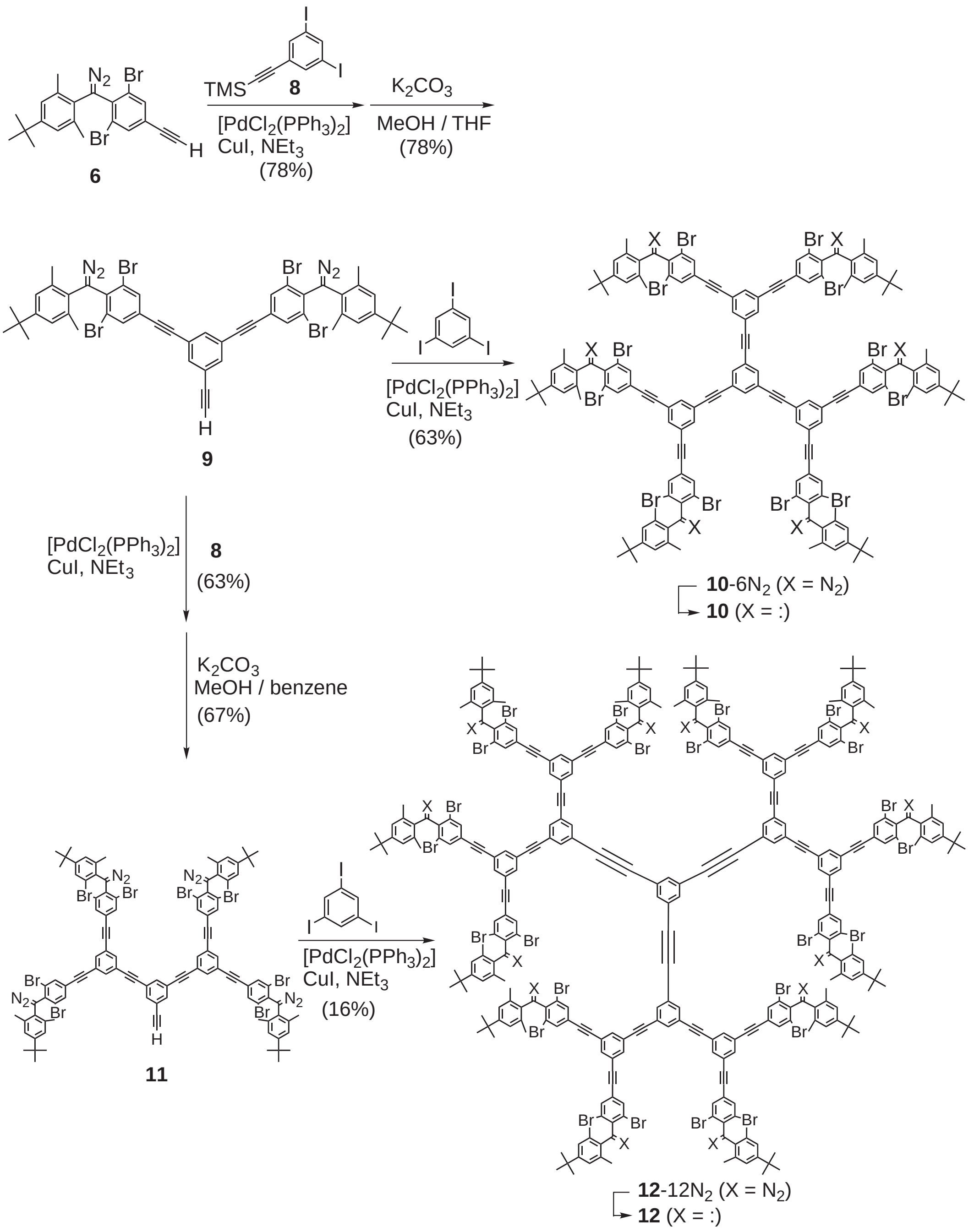
We then tried to prepare a zero monodendron by reacting 2 equivalents of **6** with a difunctional monomer. 3,5-Diiodophenyl(trimethylsilyl)acetylene (**8**)[34] was used for the convergent synthesis. Scheme 6 illustrates the chemistry used in preparing phenylacetylene dendrimers containing 6 (**10**–6N$_2$) and 12 (**12**–12N$_2$) diazo units by the convergent approach. The synthesis started by preparing a series of monodendrons **9** and **11** using a repetitive process. Thus, coupling of the aromatic diiodide (**8**) with 2 equivalents of a terminal alkyne **6** carrying a persistent triplet carbene precursor resulted in the formation of a zero-generation monodendron. The dendron was then deprotected under basic conditions to give a terminal alkyne **9** at the monodendron focal point. Two equivalents of **9** were then coupled with **8** followed by the deprotection to give the first-generation ($n = 1$) product **11** bearing four peripheral diazo units.

Instead of continuing the repetitive process further, we coupled the zero- and first-generation monodendrons (**9** and **11**, respectively) to a core, i.e., 1,3,5-triiodobenzene. The coupling took place very smoothly to afford phenylacetylene dendrimers having 6 (**10**–6N$_2$) and 12 (**12**–12N$_2$) diazo units.[32]

SQUID measurements were made for the photoproducts from hexakis (**10**–6N$_2$) and dodecakis(diazo) compounds (**12**–12N$_2$). The experimental data (M/Ms vs H/T) were fitted best with Eq. 2 with $S = 1.62$, $F = 2.85$ for hexakis(diazo), and $S = 1.62$, $F = 3.35$ for the dodecakis(diazo) compound (Fig. 4). The values are disappointingly smaller than the theoretically predicted values, $S = 6$ and 12 for **10** and **12**, respectively, even smaller than that of **7**.

The apparent smaller values can be reasonably interpreted in terms of the disjoint-non-disjoint concept based on the MO theory.[5,6] By applying this theory to our molecules, it can be explained why **7** has a septet state as the Ovchinnikov rule predicts, while **10** and **12** have lower spin states than predicted. In the case of the **7**, the three carbene units are connected to a central benzene ring in a non-disjoint manner to afford a high-spin ground state (Scheme 7). On the other hand, **10** consists of a dendritic structure, which has a bis(carbene) unit on terminal of branches. The connectivity of two carbene units within this bis(carbene) unit is non-disjoint and, hence, they interact in a ferromagnetic fashion with the spin quantum number $S = 2$. However, the connectivity between three bis(carbene) units through the central benzene ring is disjoint (Scheme 8). Consequently, each energy level of these disjoint systems is nearly degenerate. Similarly, while the connectivity of two carbene units within the bis(carbene) unit on the terminal branches in **12** is disjoint to generate $S = 2$ spin state, the connectivity between six bis(carbene) units through the core part is disjoint. Thus, there are no magnetic interactions between the bis(carbene) units through the core in **10** and **12**.

On the other hand, large F values, 2.85 and 3.35, observed for the photoproducts from **10**–6N$_2$ and **12**–12N$_2$, respectively,



Scheme 6.

indicate that more than one unit of the $S = 1.62$ spin states are formed from one mole of the diazo compounds. In other words, **10** is regarded as a species comprising of 2.85 units of $S = 1.62$ spin state, while **12** 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 8.

However, the connectivity can be changed from disjoint to non-disjoint by introducing a new spin system which disturb NBMO coefficients in the original spin systems. In the hexakis system, for instance, this is done by incorporating a new carbene unit between the bis(carbene) units and core benzene. In order to prove this idea, we prepared a model pentakis(diazo) compound where two bis(diazo) units are connected by an interior diazo group so as to make all five carbene units interact in a ferromagnetic fashion (Scheme 9). The interior diazo compound used in this study was bis(4-iodo-2,6-dimethylphenyl)diazomethane (**14**). Coupling of **14** with 2 equivalent of a bis(diazo) compound **9**[32] carrying two persistent triplet carbene precursors resulted in the formation of a desired pentakis(diazo) compound (**15**–$5N_2$)[35] under mild Sonogashira coupling reaction conditions (Scheme 10).

To confirm whether the high-spin state is observed for **15** obtained by photolysis of **15**–$5N_2$, magnetic measurements using SQUID were carried out. The M/Ms versus H/T plot was best fitted with Eq. 2 with $S = 4.4$ ($F = 0.91$) at 2.0 K and $S = 4.2$ ($F = 0.96$) at 5.0 K. Although the S values are somewhat

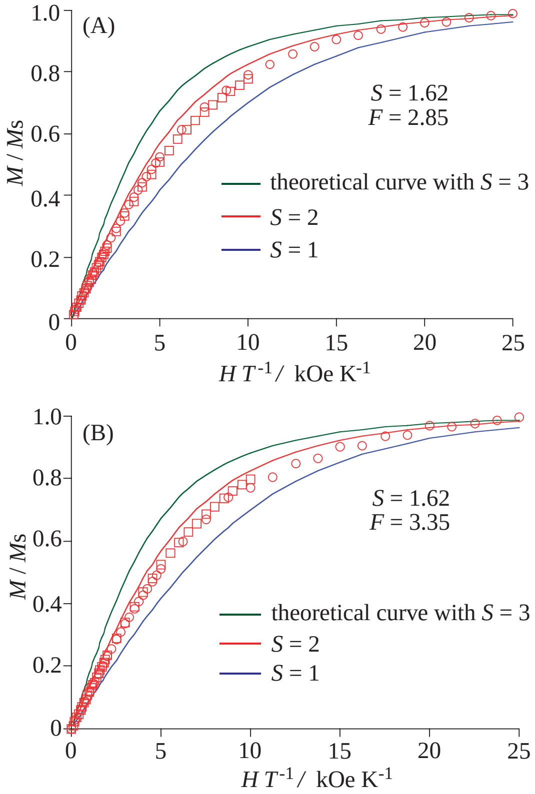
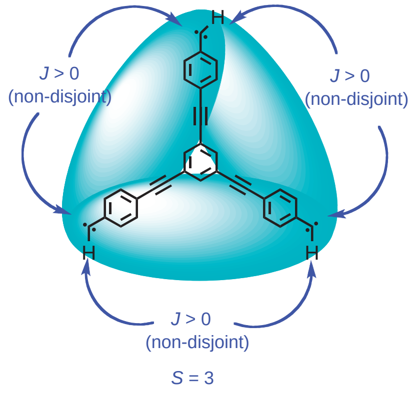


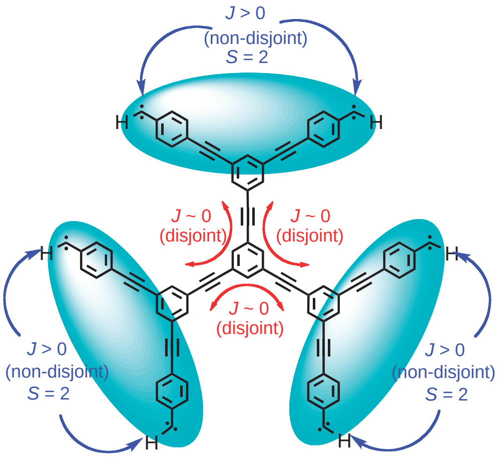
Fig. 4. Plot of magnetization (M) normalized by saturation magnetization (Ms) vs temperature-normalized magnetic field (H/T) obtained upon photolysis of (A) hexakis(diazo) compound **10**–6N$_2$ and (B) dodecakis(diazo) compound **12**–12N$_2$ measured at 2.0 and 5.0 K. Theoretical curves with $S = 1$, 2, and 3 are also indicated.



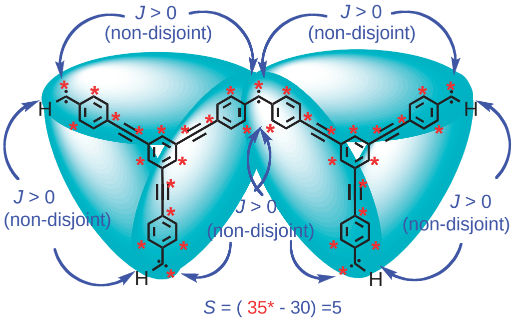
Scheme 7.

smaller than the theoretical value of 5, the results clearly indicate that the five carbene centers interact ferromagnetically. In other words, the connectivity is switched from disjoint to non-disjoint by the new carbene unit between the bis(carbene) units and core benzene.

This observation clearly demonstrates that the potential problem in the dendrimer approach to generate high-spin polycarbenes is relatively easily solved out by changing the wrong connectivity through a new carbene center in the appropriate position. The results also indicate that this is due to the persistent nature of our diazo compounds, which allows us to introduce a diazo unit at a desired position.



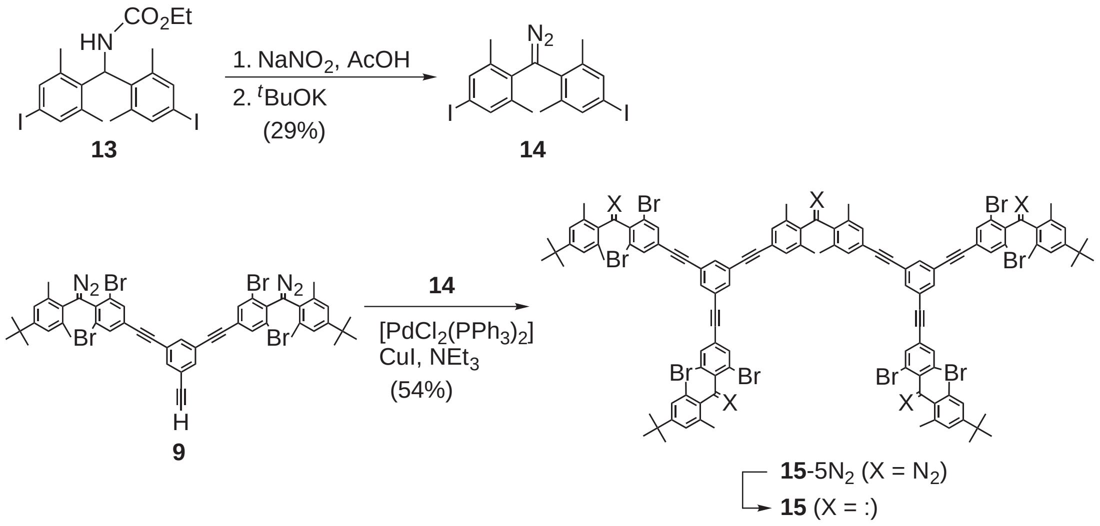
Scheme 8.



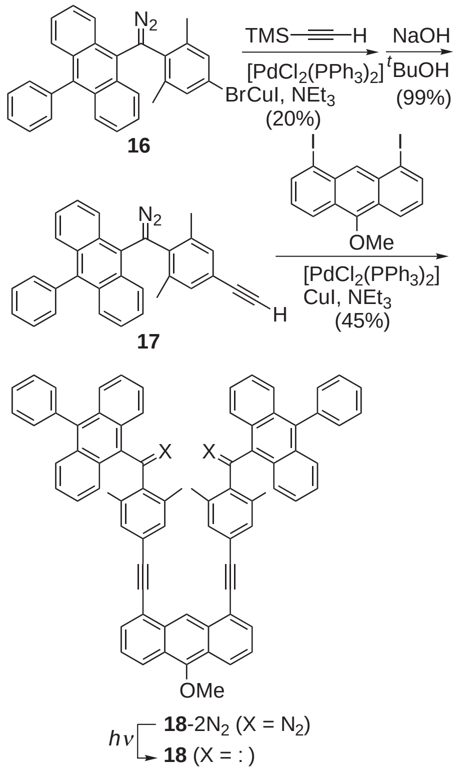
Scheme 9.

1.2 Dendrimer by Connecting Diaryldiazomethanes through Ethynyl Group on Anthracene Unit. The majority of the high-spin systems that have been investigated focused on *meta*-phenylene linkers, as in the prototypical *m*-phenylenebis(methylene).[36] It is potentially possible to use a polynuclear aromatic compound as a linker. For instance, radical centers properly introduced on anthracene rings interact ferromagnetically to generate a high-spin state.[37,38] Those polynuclear aromatic compounds have an advantage over simple aromatic rings in that they have more positions to accept spin sources. The maximum number of available positions for ferromagnetic coupling in naphthalene and anthracene are four and five, respectively, while this number is three for benzene. Thus, a spin state with a spin quantum number higher than three in one molecule can be generated by using polynuclear aromatic rings. However, almost no attempts have been made to introduce triplet carbene units on a polynuclear aromatic system. This is most probably because of the difficulty entailed in synthesizing a proper precursor. We attempted to introduce two diazo units into an anthracene unit and determine triplet carbene spin coupling through an anthracene unit.

The starting diazo compound was (4-bromo-2,6-dimethylphenyl)(10-phenyl-9-anthryl)diazomethane (**16**), which can generate a fairly persistent triplet carbene.[17,39] Treatment of **16** with trimethylsilylacetylene in the presence of palladium catalyst under mild conditions, followed by treatment with



Scheme 10.



Scheme 11.

NaOH gave (4-ethynyl-2,6-dimethylphenyl)(10-phenyl-9-anthryl)diazomethane (**17**). A bis(diazo) compound (**18**–2N_2)[40] was relatively easily prepared by coupling 2 equiv of **17** to 1,8-diiodoanthracene under mild Sonogashira coupling reaction conditions (Scheme 11).

Photolysis of the bis(diazo) compound **18**–2N_2 in a 2-MTHF solid solution was performed at 113 K in an ESR cavity with light from a high-pressure mercury lamp attached with a cut filter (λ > 350 nm). The ESR spectrum (Fig. 5) after photolysis was completely different from that observed by the photolysis of the mono(diazo) compound **17** and showed a set of structure lines at 181, 260, 299, 345, 376, and 398 mT

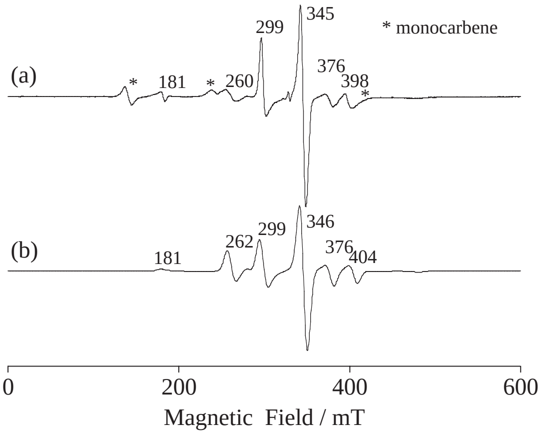
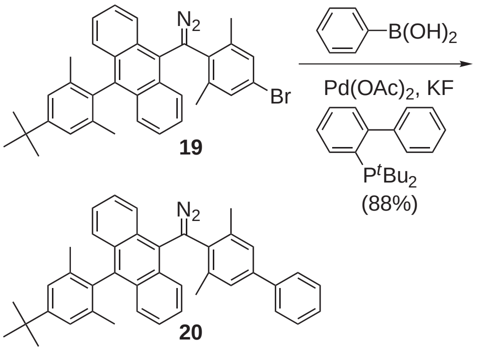


Fig. 5. (a) ESR spectra obtained by irradiation of bis(diazo) compound **18**–2N_2 in 2-MTHF at 77 K. (b) Simulated spectra of quintet bis(carbene) **18** with $S = 2$, $g = 2.003$, $D = 0.047\,\mathrm{cm}^{-1}$, and $E = 0.000\,\mathrm{cm}^{-1}$.

with rather small signal spacing. Weak signals at 140, 238, and 421 mT are similar to those observed in the photolysis of the mono(diazo) compound **17** and, hence, are attributable to the triplet monocarbene presumably formed as a result of the incomplete photolysis of the bis(diazo) compound. The smaller signal spacing observed for the major spectrum, in comparison to that for the triplet monocarbene, in consistent with the tendency that, as the spin multiplicity became higher, the D value became smaller.[41] Indeed, the major signals are reproducible by computer simulation[1d,42] employing a quintet Hamiltonian with $S = 2$, $g = 2.003$, $D = 0.047\,\mathrm{cm}^{-1}$, and $E = 0.000\,\mathrm{cm}^{-1}$. We, therefore, assigned the signals to **18**. To estimate the thermal stability of the signals, the temperature at which the quintet signals disappear was measured. Thus, the signals due to **18** started to disappear when the 2-MTHF glass containing **18** was warmed to around 130 K and disappeared completely at around 160 K. This is to be compared with that observed for septet state 1,3,5-tris(phenylmethylene)benzene, which has been shown to be persistent only up to 50 K in rigid glass.[12c] In other words, **18** is thermally stable. Note that the



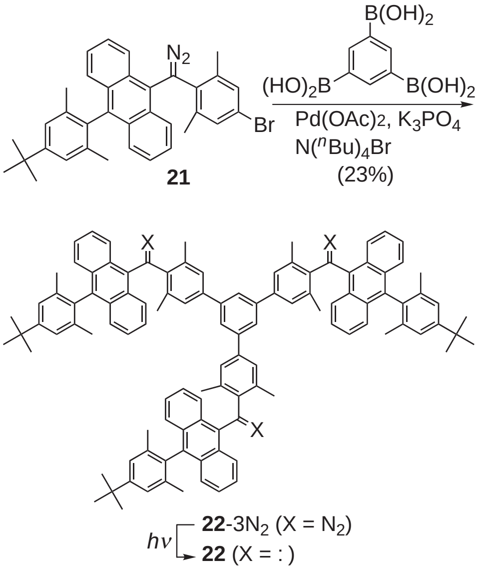
Scheme 12.

ESR signals of triplet monocarbene from **17** also decayed at around 160 K. Thus, thermal stability is not affected by this modification.

The observation shows another example in which a precursor for persistent triplet carbene can be used as a building block to construct a more complicated poly(diazo) compound that eventually generated a high-spin polycarbene with remarkably high thermal stability. It is potentially possible to introduce five diazo units at maximum on an anthracene ring so as to generate persistent pentakis(carbene) in the high-spin ground state.

1.3 Dendrimer by Connecting Diaryldiazomethanes Directly on Phenyl Groups. We found that diaryldiazomethane is stable enough to survive even the Suzuki coupling reaction.[43] This enables us to introduce the diazo unit onto a phenyl ring directly without using the ethynyl group. In this case, we used the diazo unit **19** having 10-(4-*t*-butyl-2,6-dimethylphenyl)anthryl and 4-bromo-2,6-dimethylphenyl groups, which can generate a fairly persistent triplet carbene.[17,44] In order to test the stability of the diazomethane under Suzuki coupling conditions, we first treated it with phenylboronic acid in the presence of $Pd(OAc)_2$ as a catalyst with $P(t\text{-}Bu)_2$(2-BP) (2-BP = 2-biphenylyl) as a ligand and KF as a base in tetrahydrofuran (THF) at 40 °C. The usual workup gave the desired phenylated compound (**20**–N_2) with the diazo group intact (Scheme 12). Coupling with benzene-1,3,5-triboronic acid did not work under similar conditions. However, the 1,3,5-tris(diazo) compound (**22**–$3N_2$)[45] was obtained by using tetrabutylammonium bromide and K_3PO_4, in place of the phosphine and base, respectively, in *N*,*N*-dimethylformamide (DMF) at 40 °C (Scheme 13).[46] Appreciable decomposition of the diazo group was not noted in all cases, at least under the conditions employed here.

Irradiation ($\lambda > 300$ nm) of tris(diazo) compound (**22**–$3N_2$) in 2-MTHF at 77 K gave ESR spectra (Fig. 6) that were completely different from those observed for the corresponding monocarbene from **20**. The spectra showed rather strong signals centered around ca. 335 mT. The major signals are reproducible by computer simulation[1d,41,42] employing a quintet Hamiltonian with $S = 2$, $g = 2.003$, $D = 0.015\,\text{cm}^{-1}$, and $E = 0.001\,\text{cm}^{-1}$. We, therefore, assign the signals to septet tris(carbene) **22**. The signals do not decay appreciably up to 140 K, start to decompose at around 150 K, and disappear irreversibly above 160 K.



Scheme 13.

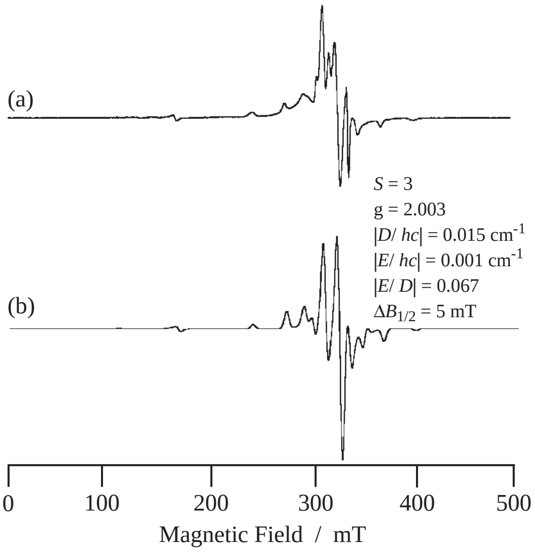
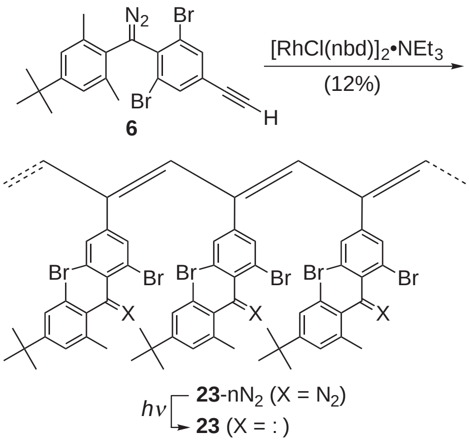


Fig. 6. (a) ESR spectra obtained by irradiation of tris(diazo) compound **22**–$3N_2$ in 2-MTHF at 77 K. (b) Simulated spectra of septet tris(carbene) **22** with $S = 2$, $g = 2.003$, $D = 0.015\,\text{cm}^{-1}$, and $E = 0.001\,\text{cm}^{-1}$.

In order to confirm whether the high-spin states observed for tris(carbene)s are in the ground state or not, magnetic measurements were carried out. The observed data for photoproducts of **22**–$3N_2$ were fitted with Eq. 2 with $S = 2.56$ and $F = 0.55$. The value is close to the theoretical value of 3, indicating that the three carbene centers interact ferromagnetically to produce a septet ground state, as was expected. Because 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. These observations unequivocally show that a persistent triplet diphenylcarbene unit incorporated into a π-network in a ferromagnetic fashion indeed acts as a spin source to generate a high-spin ground state.



Scheme 14.

2. Polymer Approach

We found that diphenyldiazomethane, from which a persistent triplet carbene can be generated, also survived under Rh-complex-catalyzed polymerization,[47,48] with the diazo group intact to give poly(phenylacetylene)s bearing diazo units.

(2,6-Dibromo-4-ethynylphenyl)(4-*t*-butyl-2,6-dimethylphenyl)diazomethane (**6**)[32] was selected as a starting material to survive the chemical manipulations required to prepare the corresponding polymer. Treatment of **6** with [$RhCl_2$(nbd)] (nbd = norbornadiene) complex in the presence of triethylamine as a cocatalyst in toluene for 1 day at room temperature followed by quenching by MeOH and filtration gave a red solid (Scheme 14).[49] The solid was dissolved in $CHCl_3$ and purified by recycled gel-permeation chromatography to obtain a main fraction. The average molecular weight of polymers (**23**–nN_2) was estimated to be approximately 86000 (190mer) from GPC calibration using a polystyrene standard. IR spectra of the polymer (**23**–nN_2) showed a strong absorption band at $2100\,cm^{-1}$ due to the C=N=N stretch of the diazo group, whose intensity relative to the other bands was essentially identical with that observed for the starting monomer **6**. This clearly indicates that the diazo group is not decayed during the polymerization process.

A 2-MTHF solution of **23**–nN_2 was placed inside the sample compartment of a SQUID and irradiated at 5–10 K with an argon ion laser ($\lambda = 488$ nm). The observed magnetization data for photoproduct for **23**–nN_2 at two different temperatures did not fit the same Brillouin function. Since the magnetization is attenuated at lower temperatures, the presence of antiferromagnetic interaction among the unpaired spins is suggested. When a sample concentration as low as 0.5 mM is taken into account, the observed antiferromagnetic interaction can be assigned to an intramolecular interaction rather than an intermolecular one. Therefore, the data at 5 K where the antiferromagnetic interaction is weaker were analyzed in terms of the Brillouin function. The data were fitted with Eq. 2 with $S = 4.90$ ($F = 0.35$). Alternatively, the data were better analyzed by a two-component Brillouin function[9d] with $S = 9.63$ ($F = 0.15$) and $S = 1.94$ ($F = 0.22$) (Fig. 7). Significantly small F values indicate either that the decomposition rate of the precursor diazo functional groups is incomplete or that there are considerable intramolecular antiferromagnetic interactions between the carbene centers. Since the IR analysis of the spent solution showed that most of the diazo groups disappeared, the latter possibility is more likely.

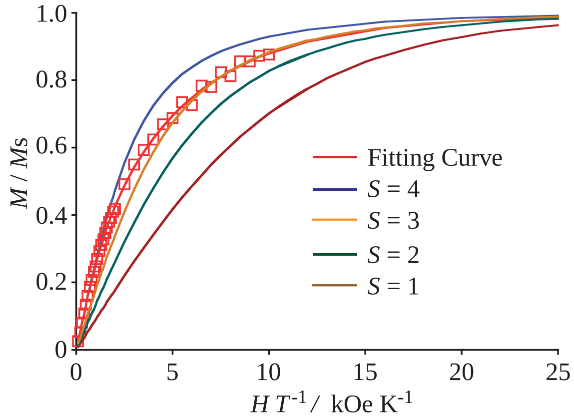
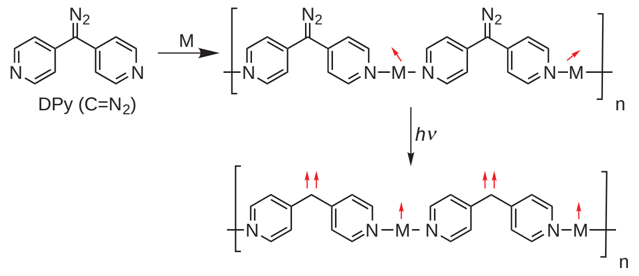


Fig. 7. Plot of magnetization (M) normalized by saturation magnetization (Ms) vs temperature-normalized magnetic field (H/T) of the photoproducts from poly(diazo) compound **23**–nN_2 measured at 5.0 K. The red line represents two-component theoretical curve with $S = 9.63$ ($F = 0.15$) and $S = 1.94$ ($F = 0.22$).

The observations suggest that a persistent triplet diphenylcarbene unit incorporated into a π-network of the phenylacetylene polymer in a ferromagnetic fashion indeed acts as a spin source to generate a high-spin ground state. However, the estimated spin multiplicities are not as high as that expected from degree of polymerization. It should be noted that the connectivity of carbene centers on the pendant phenyl group through the polyene backbone is non-disjoint in the Borden/Davidson sense,[5] and hence, the spins are expected to interact ferromagnetically. The poly(phenylacetylene)s bearing stable radical groups have been shown to have a spin multiplicity of 1/2, indicating that through-bond interaction was essentially not observed.[50] This is interpreted as indicating that the polyene structures do not have a planar polyene backbone and also that the dihedral angle between the backbone and the attached phenyl ring is significantly twisted. A defect in the backbone structure due to the nature of phenylacetylene polymerization is also suggested.[50c] A similar explanation can be applied to the unexpectedly low-spin multiplicities observed for polycarbene **23**. In this respect, π-conjugated networks that retain coplanarity are required. Poly(phenylenevinylidene)s are fully conjugated polymers with high chain stiffness.[8b,c,10c,d] High-spin polymer systems may be generated by using phenylene-ethynylene as a backbone.

It is interesting to note here that the spin multiplicity of **23** is significantly higher than that of a component spin unit, i.e., triplet carbene ($S = 1$), rather than an almost complete lack of magnetic interaction, as observed for the poly(phenylacetylene) bearing stable radical units. This is partly ascribable to the higher spin density of the present system composed of triplet carbene units than that composed of doublet radical units and demonstrates the usefulness of triplet carbene as the spin source for constructing high-spin organic molecules.



Scheme 15.

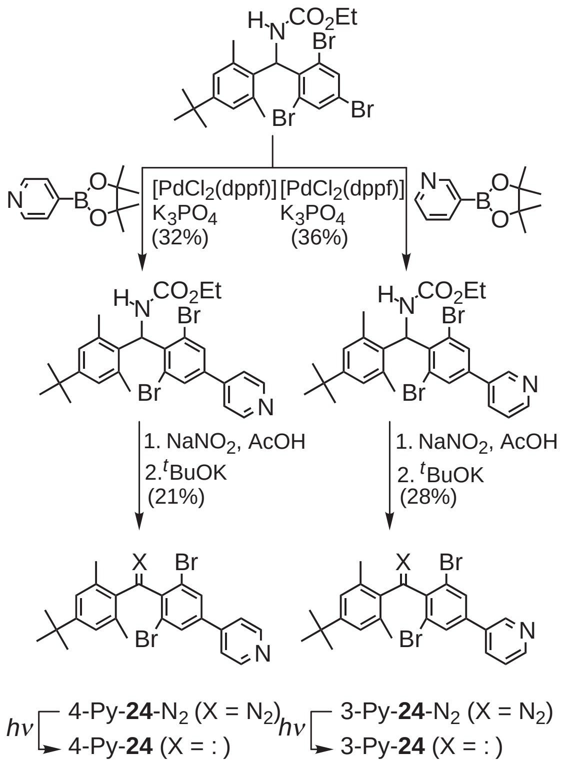
3. Hetero Spin Approach

The third approach is to utilize hetero spin systems comprising of 2p spins of organic radicals and 3d spins of magnetic metal ions.[51,52] This strategy is based on the supramolecular chemistry exhibited by pyridine– and polypyridine–metal ions.[53] For instance, magnetic interaction between radical centers and metal ions can be realized through a pyridine ligand to generate a high-spin unit. Thus, bis(4-pyridyl)diazomethane DPy(C=N$_2$) forms a polymeric chain structure by ligation with coordinatively unsaturated metal ions (M). The 3d spins on metal ions in the chain $[\text{–DPy(C=N}_2\text{)–M–}]_n$ do not interact with each other, but once triplet bis(4-pyridyl)carbene DPy(C:) is generated upon irradiation of the complex to form the carbene–metal ion complex $[\text{–DPy(C:)–M–}]_n$, they start to interact with each other through the 2p spins on the carbene center, thereby generating a high-spin system comprising 2p and 3d spins (Scheme 15).[11,51]

This suggests that if a pyridyl group is introduced on a phenyl ring of a sterically congested diphenyldiazomethane, which is a precursor for a persistent triplet carbene, a polymeric diazo compound chain should be attainable after coordination with metal ions, which will eventually result in the generation of persistent high hetero spin system.

3.1 2:1 Copper Complexes of Diphenyldiazomethanes Having a Pyridine Ligand with a Metal Ion. First of all, it needs to be confirmed whether the 2p spins of triplet carbene, generated upon photolysis of the chain, can indeed interact magnetically with the 3d spin of metal ions through the pyridyl group located remote from the carbene center. If so, the overall magnetic properties will also be affected by the position of the coordinating nitrogen in the pyridine ring. In order to examine these issues, we have prepared diphenyldiazomethanes having pyridyl groups and have characterized the magnetic properties of the photoproducts formed from these diazo compounds.

Compound **1**, which can generate a fairly persistent triplet diphenylcarbene,[54] was used. Before preparing the desired precursor, the spin densities of organic spin sources need to be considered. The nonbonding molecular orbitals (NBMOs) of the triplet carbene were studied using the simple Hückel molecular orbital method, in which the atoms having nonzero NBMO coefficients have been starred. To a first approximation, the spin densities are assumed to be generated on the atoms with such nonzero coefficients. Thus, ligand pyridyl groups need to be introduced at the ortho and/or para positions, which have NBMO spin densities such that the interactions of the spins are transmitted effectively to a ligand.[5,6] We decided to introduce pyridyl groups at the para position of **1** for synthetic reasons (Scheme 16).



Scheme 16.

The spin densities at the bridging groups are also important factors to take into account. The nonbonding molecular orbitals (NBMOs) of the isomeric carbenes 3- and 4-pyridylcarbenes suggest that, while in the para isomer 4-pyridylcarbene, nonzero NBMO coefficients are expected to be on the pyridyl nitrogen, zero NBMO coefficients are expected on the pyridyl nitrogen atom in the meta isomer 3-pyridylcarbene. This suggests that the magnitude of the spin interactions in the complex between 3-pyridylcarbene and metal ions is expected to be small. The sign of the spin polarization of the π-electrons on the nitrogen atom is also different between the two isomers (see below).

These factors will affect the overall spin states if the 2p and 3d spins interact magnetically. In order to test this idea, we prepared sterically congested diphenyldiazomethanes having a 3- and 4-pyridyl groups (3- and 4-Py–**24**–N$_2$, respectively) as a ring substituent and characterized the magnetic properties of the complex formed as a result of coordination to Cu$^{\text{II}}$ ions followed by irradiation. Coordination of the pyridyl ligand of 4-Py–^{3}**24** to a Cu$^{\text{II}}$ ion induces a ferromagnetic exchange interaction, due to a spin polarization mechanism and the interaction arising from the orthogonal relationship of singly occupied $d_{x^2-y^2}$ orbitals on the Cu$^{\text{II}}$ ion with the π-orbitals on the nitrogen atom of the pyridine. On the other hand, the sign of the polarization of the π-electrons on the nitrogen atom for 3-Py–^{3}**24** may be opposite to that of 4-Py–^{3}**24**. Therefore, an antiferromagnetic interaction should be induced between the carbene center and the copper ion in this case.

The desired diazo compounds were prepared by using Suzuki coupling reaction. Thus, the precursory carbamate

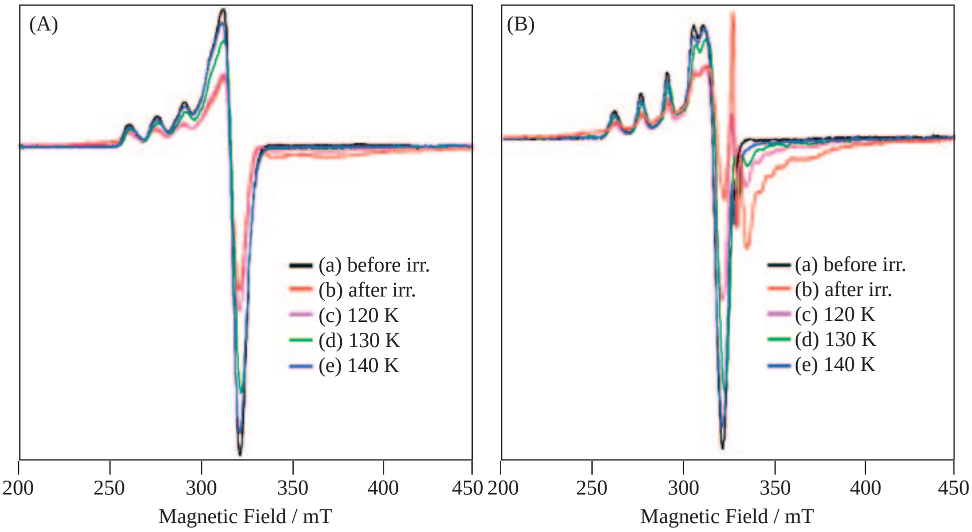


Fig. 8. ESR spectra obtained by irradiation of (A) 4-Py–**24**–N_2 and [Cu(hfac)$_2$] in 2-MTHF mixed in a 2:1 molar ratio and (B) 3-Py–**24**–N_2 and [Cu(hfac)$_2$] in 2-MTHF mixed in a 2:1 molar ratio: (a, b) ESR spectra before (a) and after (b) irradiation ($\lambda > 350$ nm) at 77 K; (c–e) ESR spectra observed at 77 K after warming the matrix to (c) 120, (d) 130, and (e) 140 K.

was coupled with the pyridylboronate to give ethyl (4-*t*-butyl-2,6-dimethylphenyl)[2,6-dibromo-4-(3- or 4-pyridyl)phenyl]-methylcarbamate, which was converted to the corresponding diazo compounds (3- and 4-Py–**24**–N_2) by a routine method (Scheme 16).[55]

A solution of 4-Py–**24**–N_2 (13.6×10^{-3} M) in 2-MTHF and bis(hexafluoroacetylacetonato)copper(II) [Cu(hfac)$_2$] (6.8×10^{-3} M) in 2-MTHF were mixed at a 2:1 molar ratio at room temperature, and the mixture was allowed to stand overnight. The solution showed ESR signals at 260, 275, 291, 312, and 321 mT, which are characteristic of the magnetic orbital $d_{x^2-y^2}$ in the Cu^{II} ion of [Cu(hfac)$_2$][56] before irradiation. After irradiation ($\lambda > 350$ nm) of the solution at 77 K, broad signals at around 331 mT that were completely different from those observed for the corresponding monocarbene (4-Py–**24**) appeared at the expense of the signals due to the isolated Cu^{II} ion in [Cu(hfac)$_2$] (Fig. 8A). The original signals due to Cu^{II} were recovered when the sample was warmed to room temperature and recooled. The observation that no significant signals due to isolated triplet carbene 4-Py–**24** were observed suggests that the pyridine moiety binds with [Cu(hfac)$_2$] essentially in a nearly quantitative manner under these cryogenic conditions.

To estimate the thermal stability of the signals, the sample was warmed to a desired temperature. The new signals started to disappear at 120 K but were observable up to 130 K. The signals were replaced by those due to the Cu^{II} ion at around 140 K.

After irradiation of 2:1 mixture of the meta isomer 3-Py–**24**–N_2 and [Cu(hfac)$_2$] at 77 K, rather sharp ESR signals due to the 3-Py–**24**–Cu complex at 325–354 mT appeared at the expense of the signals due to the isolated Cu^{II} ion (Fig. 8B). The shape of the signals is completely different from that observed for the 4-Py–^{3}**24**-Cu^{II} complex. Upon warming the matrix, the sharp signals started to decrease at around 120 K and were replaced by those due to the Cu^{II} ion at around 140 K. Although the spectral changes upon irradiation of the Py–**24**–N_2–Cu complexes differed between the two isomers, they were not clear enough to judge the difference in the mode of magnetic interaction.

To obtain the spin quantum numbers of the Py–**24**–Cu complex, magnetic measurements were carried out. The experimental data in this case were analyzed by best-fitting the Brillouin function $B(x)$ as given by Eq. 3:[33]

$$\begin{aligned} M &= M\mathrm{a} - M\mathrm{b} = F(M_{\mathrm{comp}} - M_{\mathrm{Cu}}) \\ &= F\{Ng\mu_{\mathrm{B}}SB(x) - Ng'\mu_{\mathrm{B}}B(x')/2\}, \end{aligned} \tag{3}$$

where M_{comp} and M_{Cu} are the magnetization due to the carbene–Cu complexes and the diazo–copper complexes, respectively, $x = gS\mu_{\mathrm{B}}H/(k_{\mathrm{B}}T)$, $x' = g'\mu_{\mathrm{B}}H/(2k_{\mathrm{B}}T)$, and the other symbols have their usual meaning.

The observed data for the photoproducts of diazo–copper complex (4-Py–**24**–N_2–Cu) were fitted with Eq. 3 with $S = 2.01$ and $F = 0.82$. The estimated S value was thus slightly lower than the theoretical one for when two carbene centers ($S = 2$) interact with a copper(II) ion ($S = 1/2$) ferromagnetically ($S = 2.5$). The lower S value is probably due to a carbene defect arising from incomplete photolysis of the diazo compounds or decomposition of carbenes. The overall results for the field-dependence of M for the complex of [Cu(hfac)$_2$] with 4-Py–**24** suggest that the generated carbene centers interact ferromagnetically with copper(II) ions, as was expected.

The magnetization data obtained after irradiation of the 2:1 3-Py–**24**–N_2–copper complex, on the other hand, were analyzed by a fitting curve with $S = 1.00$ and $F = 0.60$. Although this value corresponds to the theoretical one for magnetically isolated carbene 3-Py–**24**, it is notable that the saturation magnetization corresponds to only 29% of that expected for magnetically isolated carbene. Thus, the low S and Ms values can be explained in terms of the antiferromagnetic interaction between the carbene centers and the copper ion in the complex.

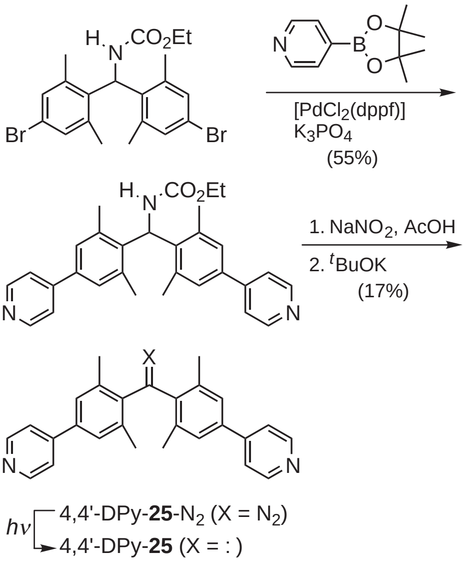
These results demonstrate that a ferromagnetic interaction is observed for the copper ion complex with the 4-pyridyl isomer, while an antiferromagnetic interaction is observed in the corresponding 3-pyridyl isomer. In other words, the 2p spins of the triplet carbene indeed interact magnetically with the 3d spin of metal ions through the pyridyl group located remote from the carbene center.

3.2 Copper Complexes of Diphenyldiazomethanes Having Two Pyridine Ligands. The next step is to apply this method to prepare a longer chain by introducing two pyridyl units on diaryldiazomethanes and to confirm whether actually high-spin and persistent polycarbene can be generated by photolysis of the complex. We prepared diphenyldiazomethanes having two pyridyl groups and characterized magnetic properties of the photoproducts from their complex with metal ions.

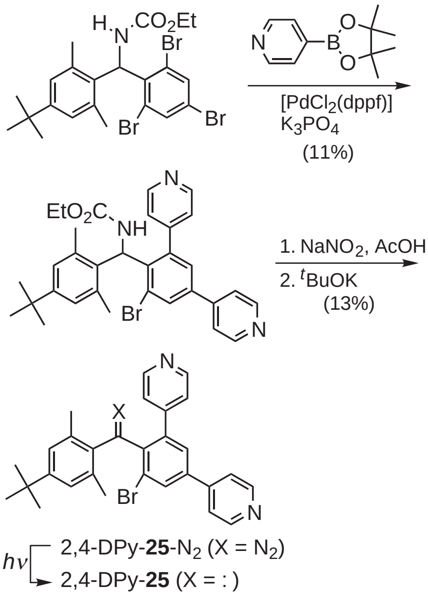
Diphenyldiazomethanes (DPy–**25**–N_2) having two pyridyl groups, i.e., bis[2,6-dimethyl-4-(4-pyridyl)phenyl]diazomethane (4,4′-DPy–**25**–N_2) and [2-bromo-4,6-di(4-pyridyl)phenyl]-(4-*t*-butyl-2,6-dimethylphenyl)diazomethane (2,4-DPy–**25**–N_2), were prepared by a routine method (Schemes 17 and 18).[57]

Both diazo compounds are expected to form a chain as a result of complexation with metal ions (to form –DPy–**25**–N_2–M–), and the chain is expected, upon irradiation, to generate a polycarbene chain (–DPy–**25**–M–) in which the spins on the chain start to interact ferromagnetically. However, there is a potential difference between the two in the connectivity of the ferromagnetic coupling unit with respect to carbene centers (Scheme 19). In the –4,4′-DPy–**25**–M– chain, for instance, carbene centers are involved in coupling units in the chain (Class 1 in Scheme 19), while in the –2,4-DPy–**25**–M– chain, carbenes are attached as pendants to a coupling unit of the chain (Class 2 in Scheme 19). It has been pointed out that, in the linear connectivity (Class 1), there is a fundamental problem associated with the presence of only one exchange pathway (through the π-system) between any two remote radical or carbene sites.[9b] Therefore, a failure to generate a carbene in the interior of the chain may interrupt the exchange pathway. One way to avoid this problem is to introduce a carbene unit as a pendant to a coupling unit of polymer backbone (Class 2). In other words, failure to generate a carbene (a chemical defect) in the interior of a polycarbene chain may interrupt the exchange pathway in the former, while this chemical defect may be circumvented in the latter.[58,59]

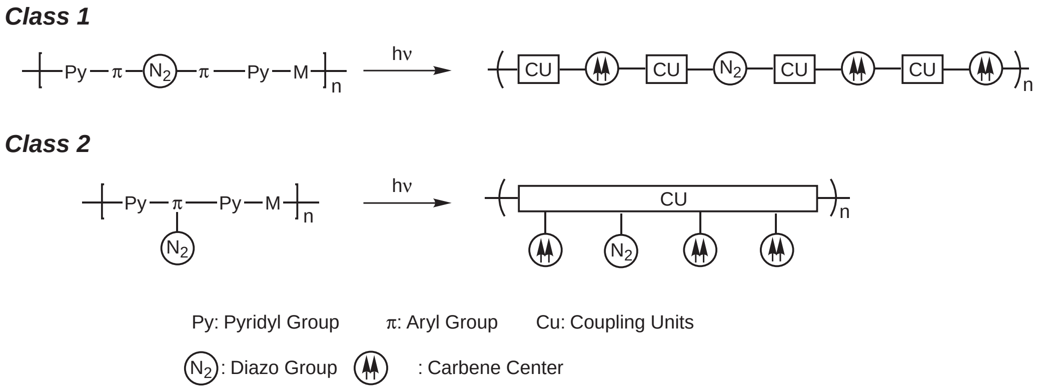
A solution of 4,4′-DPy–**25**–N_2 and [Cu(hfac)$_2$] mixed in a 1:1 molar ratio (3.3×10^{-3} M) in 2-MTHF was allowed to stand overnight and was used without purification. The solution showed ESR signals due to Cu^{II} ion[56] in [Cu(hfac)$_2$] at 77 K before irradiation (Fig. 9Aa). When the solution was irradiated at 77 K, rather strong and broad signals gradually ap-



Scheme 17.



Scheme 18.



Scheme 19.

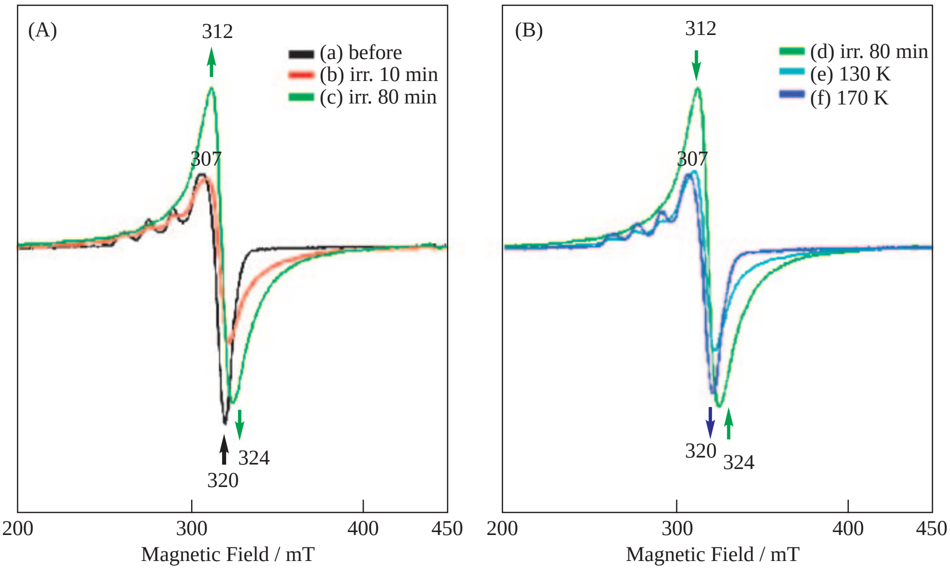


Fig. 9. ESR spectra obtained by irradiation of 4,4′-DPy–**25**–N_2 and $[Cu(hfac)_2]$ in 2-MTHF mixed in a 1:1 molar ratio. (A) (a–c) ESR spectrum before (a) and after irradiation ($\lambda > 350$ nm) at 77 K for 10 (b) and 80 min (c). (B) (e and f) ESR spectra observed at 77 K in 2-MTHF after warming the matrix to (e) 130 and (f) 170 K.

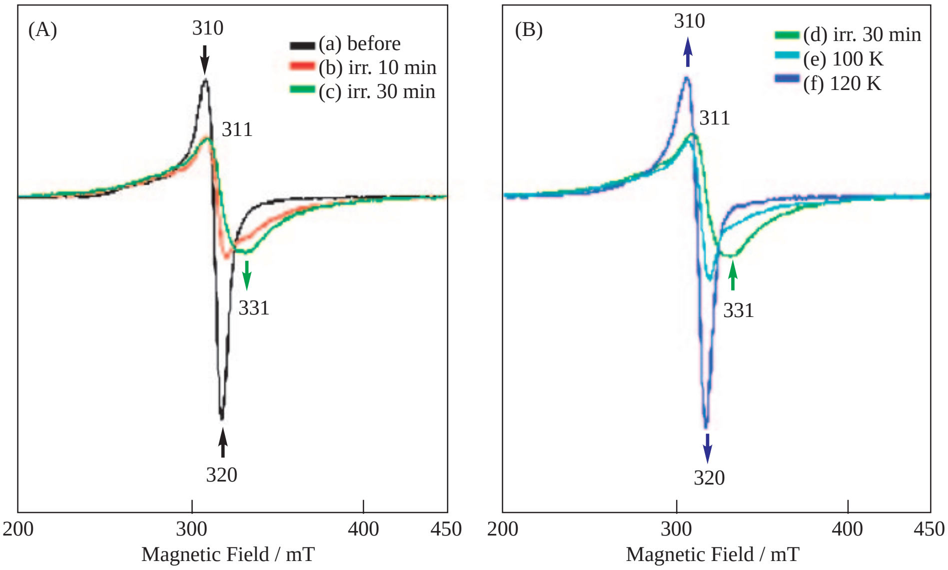


Fig. 10. ESR spectra obtained by irradiation of 2,4-DPy–**25**–N_2 and $[Cu(hfac)_2]$ in 2-MTHF mixed in a 1:1 molar ratio. (A) (a–c) ESR spectrum before (a) and after irradiation ($\lambda > 350$ nm) for 10 (b) and 30 min (c) at 77 K. (B) (e and f) ESR spectra observed at 77 K in 2-MTHF after warming the matrix to (e) 100 and (f) 120 K.

peared at 312 and 324 mT at the expense of the signals due to isolated Cu^{II} ion in $[Cu(hfac)_2]$ unit and replaced the signal due to Cu^{II} ion after 80 min irradiation (Figs. 9Ab and 9Ac). No significant signals due to isolated triplet carbene 4,4′-DPy–^{3}**25** were observed, suggesting that the pyridine moiety binds with $[Cu(hfac)_2]$ essentially in quantitative manner under cryogenic conditions.[51a,52] In order to estimate the thermal stability of the signals, the sample was warmed to a certain temperature, allowed to stand at this temperature for 5 min and recooled to 77 K to measure ESR signals. The new signals started to disappear at 130 K but were observable up to 150 K. The signals were replaced by those due to Cu^{II} ion at around 170 K (Figs. 9Bd–9Bf).

Irradiation of 1:1 complex of 2,4-Dpy–**25**–N_2 and $[Cu(hfac)_2]$ (2.4×10^{-3} M) gave somewhat different results. The spectrum of the solution before irradiation showed only broad ESR signals at 310 mT without showing characteristic of Cu^{II} ion of $[Cu(hfac)_2]$ (Fig. 10Aa). This is most probably because 3d spins on Cu^{II} ions in the complex can already interact each other through pyridyl aromatic π-networks since they are involved in the ferromagnetic chains. Upon irradiation, the signals started to decrease with concomitant shift of the signal maximum until it reached a plateau at 330 mT after irradiation for 0.5 h (Figs. 10Ab and 10Ac). Again, the fact that no significant signals due to isolated triplet carbene 2,4-DPy–^{3}**25** were observed suggested that the pyridine moiety binds to

[Cu(hfac)$_2$] in nearly quantitative manner under cryogenic conditions. Upon warming the matrix containing the sample, the new signals gradually disappeared and the original signals before irradiation recovered at 120 K (Figs. 10Bd–10Bf). It is to be noted here that the signals of bis(4-pyridyl)carbene–[Cu(hfac)$_2$] disappeared irreversibly at temperature higher than 60 K,[52d] meaning DPy–**25**–Cu complex has remarkable thermal stability.

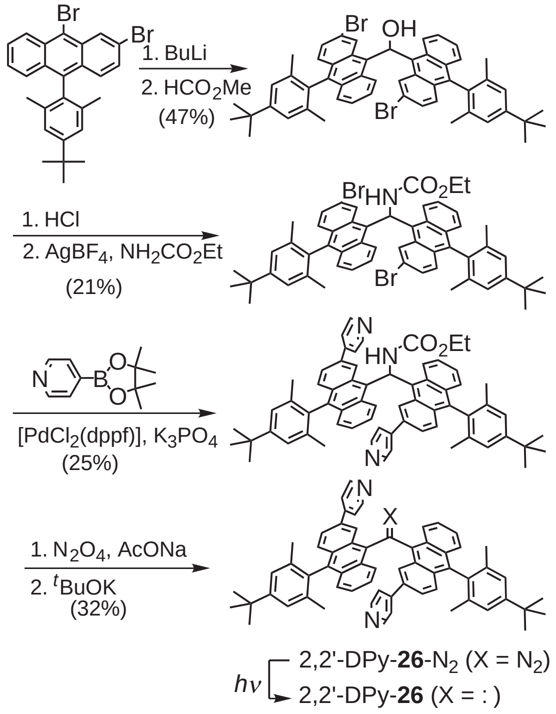
To determine the spin quantum numbers of the polycarbene bridged by copper ions, the magnetic properties were studied. A 2-MTHF solution of 4,4′-DPy–**25**–N$_2$–copper (1:1) complex was irradiated at 5–10 K with a light ($\lambda = 488$ nm) with an Ar ion laser. The field dependence of magnetization generated by irradiation for the complex was analyzed in terms of the Brillouin function. The experimental data in this case were analyzed by best-fitting the Brillouin function $B(x)$ as given by Eq. 4.[1c,33,52] The observed data were fitted with Eq. 4 to give spin quantum number $S = 6.80$ and $F = 0.60$ at 2.0 K. The values were found to be somewhat temperature dependent, S/F being 6.43/0.58 and 5.90/0.46 at 3.0 and 5.0 K, respectively. The value of $\chi_{\mathrm{mol}}T$ increased with decreasing temperature from 70 to 4 K. This indicates that J/k is small but positive, suggesting the presence of intramolecular ferromagnetic interaction.

$$\begin{aligned} M &= M\mathrm{a} - M\mathrm{b} = M_{\mathrm{comp}} - M_{\mathrm{Cu}} \\ &= Ng\mu_{\mathrm{B}}\{SB(x) - B(x')/2\}. \end{aligned} \tag{4}$$

The experimental data (M vs H/T) for 2,4-DPy–**25**–N$_2$–copper complex after irradiation were analyzed in terms of Eq. 4 with fitting curve with $S = 3.71$ and $F = 0.73$. The values were again found to be somewhat temperature dependent, S/F being 3.31/0.72 and 2.85/0.72 at 3.0 and 5.0 K, respectively.

These results demonstrate that a high-spin species is actually generated as the photoproduct of a copper ion complex with sterically congested diaryldiazomethanes having a 4-pyridyl group as a result of ferromagnetic interaction between 3d spin of metal ions and 2p spins of triplet carbene through the pyridyl group located remote from the carbene center. The complexed carbene showed significant stability surviving up to 120–150 K in 2-MTHF, while analogous copper ion complexes with unprotected pyridylcarbene ligands decay at temperature higher than 60 K.[52d] The observations suggest that it is potentially possible to prepare a persistent high-spin polycarbene by extending this method.

3.3 Copper Complexes of Dianthryldiazomethanes Having Two Pyridine Ligands. We then chose bis[10-(4-*t*-butyl-2,6-dimethylphenyl)-9-anthryl]carbene (**26**) as a triplet carbene unit to construct a high hetero-spin system since this carbene has the longest lifetime (over 10 days) in solution at room temperature.[17b] Thus, we needed to introduce pyridyl groups onto the precursor of **26**, that is, bis[10-(2,6-dimethyl-4-*t*-butylphenyl)-9-anthryl]diazomethane **26**–N$_2$. Before preparing the desired precursor, the spin densities of organic spin sources and connecting ligands need to be considered. A pyridyl group ligand needs to be introduced on a carbon which has non-bonding molecular orbital (NBMO) spin densities.[5,6] The π-spin density distribution of triplet anthrylcarbene calculated using PM3 show that the largest spin density is at position 10. However, it is likely that aryl groups at this position are not in the same plane as the anthryl group, due to repulsion by peri hydrogens. Positions 2 (and 7) and 4 (and 5) have also significantly high spin densities, but from a synthetic standpoint, position 2 (and 7) is more realistic.



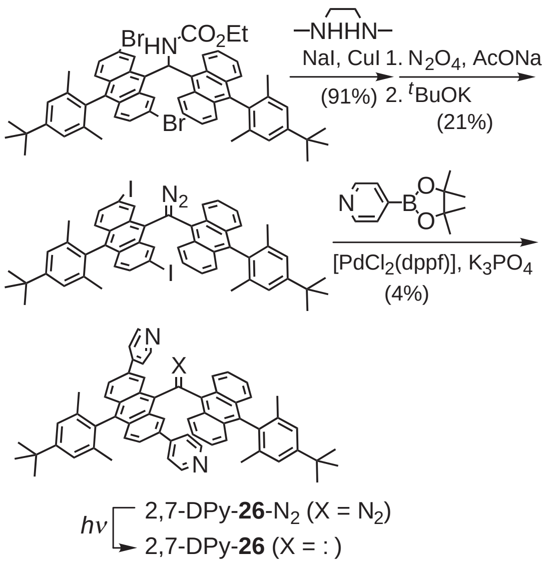
Scheme 20.

Based on the above considerations, we decided to prepare two dianthryldiazomethanes having two pyridyl groups either at the 2,2′- or the 2,7-positions, i.e., bis[10-(4-*t*-butyl-2,6-dimethylphenyl)-2-(4-pyridyl)-9-anthryl]diazomethane (2,2′-DPy–**26**–N$_2$) and [(10-(4-*t*-butyl-2,6-dimethylphenyl)-9-anthryl)][(10-(4-*t*-butyl-2,6-dimethylphenyl)-2,7-di(4-pyridyl)-9-anthryl)diazomethane (2,7-DPy–**26**–N$_2$). In the –2,2′-DPy–**26**–M– chain, for instance, carbene centers are involved in coupling units in the chain (Class 1 in Scheme 19), while in the –2,7-DPy–**26**–M– chain, carbenes are attached as pendants to a coupling unit of the chain (Class 2 in Scheme 19).[60]

Suzuki coupling reaction of the precursory carbamate took place smoothly to give ethyl bis[10-(4-*t*-butyl-2,6-dimethylphenyl)-2-(4-pyridyl)-9-anthryl]methylcarbamate, which was converted to the corresponding diazomethane (2,2′-DPy–**26**–N$_2$) by a routine method (Scheme 20).

Diazomethane 2,7-DPy–**26**–N$_2$ was prepared by the coupling reaction of the corresponding iodinated diazo compound with 4-pyridylboronate (Scheme 21).

ESR spectra on the photoproducts from the reaction of DPy–**26**–N$_2$ (11.6×10^{-3} M) in 2-MTHF and [Cu(hfac)$_2$] (11.6×10^{-3} M) in 2-MTHF showed essentially identical spectral features as those observed for the corresponding phenyl analogues. Thus, a 1:1 molar ratio mixture of 2,2′-DPy–**26**–N$_2$ and [Cu(hfac)$_2$] showed ESR signals due to the magnetic orbital $\mathrm{d}_{x^2-y^2}$ of the Cu$^{\mathrm{II}}$ ion[56] of [Cu(hfac)$_2$] before irradiation. When the solution was irradiated ($\lambda > 350$ nm) at 77 K, the signals due to the isolated Cu$^{\mathrm{II}}$ ion in the [Cu(hfac)$_2$] unit started to de-



Scheme 21.

crease, and rather broad signals gradually appeared at 340 mT, with a sharp one at 314 mT at the expense of the Cu^{II} signals, suggesting that the generated carbene centers interacted magnetically with the Cu^{II} ion to form a high-spin species.[51a,52]

Similar irradiation of the 1:1 complex of 2,7-DPy–**26**–N_2 and [Cu(hfac)$_2$] gave somewhat different results. Before irradiation, the solution showed only broad ESR signals at 309 and 319 mT, without showing the characteristic signal of the Cu^{II} ion of [Cu(hfac)$_2$]. Upon irradiation, the signal at 309 mT started to increase with a concomitant shift of the signal maximum until the maximum stopped growing at 315 mT. However, after an initial decrease in the signal at 319 mT, but it increased with a concomitant shift of the signal, until it reach a maximum at 325 mT, after irradiation for 1 h. Upon warming the matrix containing the sample, the new signals gradually decreased, and the original signals reappeared at 300 K.

To determine the spin quantum numbers of the polycarbene bridged by copper ions, the magnetic properties were studied. The experimental data were fitted to the theoretical Eq. 4 to give spin quantum number $S = 2.44 \pm 0.04$ and F (generation factor for carbene obtained from saturated magnetization) $= 0.82$ (dotted line in Fig. 11). Alternatively, the data were better analyzed by a two-component Brillouin function with $S = 3.18 \pm 0.07$ ($F = 0.66$) and $S = 0.02 \pm 0.002$ ($F = 0.23$) (solid curve in Fig. 11). This may mean that defects due to incomplete photolysis produce mixtures of the spin systems in the chains. 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 high-spin state is considered to be a ground state.

The temperature dependence of the molar paramagnetic susceptibility before and after irradiation, (χ_{molb} and χ_{mola}, respectively) in the range of 2–70 K was measured at a constant field of 5 kOe. χ_{mol} $(=\chi_{\mathrm{mola}} - \chi_{\mathrm{molb}})T$ versus T plots are shown in Fig. 12. The value of $\chi_{\mathrm{mol}}T$ increased with a decreasing temperature from 70 to 4 K. This indicates that J/k is small but positive, suggesting the presence of intramolecular ferromagnetic interaction.

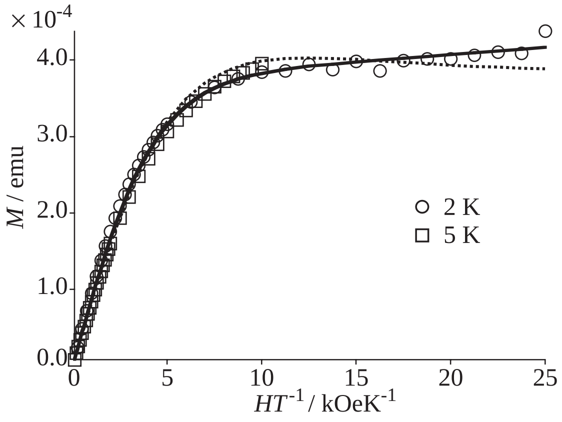


Fig. 11. Plot of M vs H/T of the photoproduct from a 1:1 mixture (1.0×10^{-3} M) of 2,7-DPy–**26**–N_2 and [Cu(hfac)$_2$] measured at 2.0 and 5.0 K in 2-MTHF. Fitting data are shown as broken (one component) and solid (two components) lines.

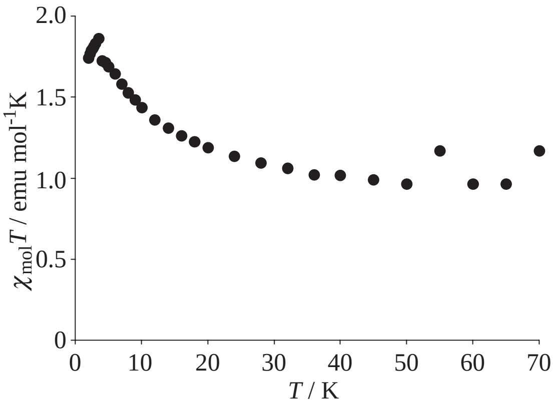


Fig. 12. Temperature dependence of the observed $\chi_{\mathrm{mol}}T$ for the photoproduct from a 1:1 mixture (1.0×10^{-3} M) of 2,7-DPy–**26**–N_2 and [Cu(hfac)$_2$] obtained at a field of 5 kOe.

The data obtained for photoproducts from similar irradiation of the 2-MTHF solution of the 1:1 2,2′-DPy–**26**–N_2–copper complex (1.0 mM) were also analyzed by the Brillouin function. The experimental data (M vs H/T) for the 2,2′-DPy–**26**–N_2–copper complex after irradiation were analyzed in terms of Eq. 4 with the fitted curve giving $S = 2.12 \pm 0.03$ and $F = 0.41$. Alternatively, the data were better analyzed by the two-component Brillouin function which produced $S = 2.70 \pm 0.13$ ($F = 0.33$) and $S = 0.49 \pm 0.24$ ($F = 0.11$). χ_{mol} $(=\chi_{\mathrm{mola}} - \chi_{\mathrm{molb}})T$ versus T plots showed that the value of $\chi_{\mathrm{mol}}T$ increased with decreasing temperature from 70 to 4 K, again suggesting the presence of intramolecular ferromagnetic interaction.

It should be noted that the S and F values observed for the photoproduct of the 1:1 2,2′-DPy–**26**–N_2–copper complex are notably smaller than those for that of the 1:1 2,7-DPy–**26**–N_2–copper complex. Incomplete photolysis of diazo groups is often pointed out as a reason for rather small S and F values. However, almost complete photolysis of the sample was confirmed, by taking the difference in absorption at 2040 cm^{-1} due to the diazo moieties before and after SQUID measurements. It may be that there is a defect in the ligation of pyridine groups in the 2,2′-DPy–**26**–N_2–copper complex. This is in accord with the observation that in the ESR experiments on the photoproduct of the 2,2′-DPy–**26**–N_2–copper complex, the signals due to free copper ions did not disappear completely. If there are partially uncoordinated copper ions in the complex, the magnetic contribution of the uncoordinated copper ions will be deleted in the equation $M_{\mathrm{comp}} - M_{\mathrm{Cu}}$, and this will result in small S and F values.

The results again demonstrate that high-spin species are generated as the photoproduct of a copper ion complex with sterically congested diaryldiazomethanes having a 4-pyridyl group, as a result of ferromagnetic interaction between the 3d spin of metal ions and the 2p spins of triplet carbene through the pyridyl group located remote from the carbene center. The complexed carbene showed remarkable stability, surviving up to 300 K in 2-MTHF.

Conclusion

We have found that diazomethanes that are precursors for stable triplet carbenes are also stable. This suggested that we would be able to construct a more complicated poly(diazo) compound by using diazomethane derivatives as a building block and that persistent high-spin polycarbenes would be obtained by irradiation of the poly(diazo) compounds. We have used three approaches to prepare poly(diazo) compounds.

The dendrimer approach has a potential problem in terms of the connectivity of spin units through π-networks, but this is solved by improving the wrong connectivity through a new carbene center introduced at the appropriate position. This approach also allows us to use a polynuclear aromatic compounds, such as anthracene as a linker, which have an advantage over simple aromatic rings in that they have more positions to accept spin sources. This is realized by the persistent nature of our diazo compounds, which allows us to introduce a diazo unit at a desired position on the anthracene.

Our diazomethanes are shown to survive polymerization conditions to give poly(phenylacetylene)s having pendant diazo functional groups intact. The estimated spin multiplicities of the photoproducts from the polymer are not as high as expected, based on the degree of polymerization, probably due to the lack of the co-planarity of π-networks. This problem can be solved by introducing triplet carbene units in fully conjugated polymers with high chain stiffness. Nevertheless, the spin multiplicity is significantly higher than that of a component spin unit, i.e., triplet carbene ($S = 1$), which is to be compared with an almost complete lack of magnetic interaction observed for the poly(phenylacetylene) bearing stable radical units. This is partly ascribable to the higher spin density of the present system composed of triplet carbene units than that composed of doublet radical units and demonstrates the usefulness of a triplet carbene as the spin source for constructing high-spin organic molecules.

The hetero-spin approach is also shown to be equally promising since high-spin species are generated in the photoproduct of a copper ion complex with sterically congested diaryldiazomethanes having a 4-pyridyl group, as a result of ferromagnetic interaction between the 3d spin of metal ions and the 2p spins of triplet carbene through the pyridyl group located remote from the carbene center. The spin quantum number obtained by Brillouin function analysis of the field dependence of magnetization is not very high. Delocalization of spin is an important factor. It has been shown that spin coupling is weaker for π-conjugated bis(aminoxyl)s than their carbon counterparts because spin density is localized on the aminoxyl moiety in π-conjugated aminoxyls. Significantly small D values observed for dianthrylcarbenes suggest that the unpaired electrons are extensively delocalized into two anthryl rings. Although the spin density builds up at the 2 (and 2′) and 7 (and 7′) positions, where ligands are connected, the spins are significantly dispersed in the ring carbons and hence the net spin densities on 2 (and 2′) and 7 (and 7′) carbon atoms in triplet dianthrylcarbenes are actually not large. Then, the density is further diminished in the conduit of the pyridine ring until the spins are transmitted onto the pyridine nitrogen atoms, due to partial localization on the ortho carbon atoms and possible twisting of the pyridyl rings from the plane of the anthryl ring. These factors can explain the rather small S observed for the present system compared to that of the 1:1 complex between bis(4-pyridyl)carbene and copper ions.[52] In this respect, sterically congested bis(4-pyridyl)carbene or triplet bis(9-acridyl)carbene is a more promising candidate for realizing persistent high-spin species consisting of 2p spins of carbene and 3d spins of metal ions.

An advantage of the present approach is its easiness to increase the dimension of the spin network. Koga and co-workers have increased the dimension of the spin networks from one- to two- and three-dimensional structures by using highly branched ligand containing diazo units. For instance, a high-spin carbene–copper ion complex with an S value higher than 1000 was obtained by photolysis of 3:2 complex of $[\mathrm{Cu(hfac)_2}]$ and 1,3,5-tris[diazo(4-pyridyl)methyl]benzene.[52b]

Attempts to prepare a stable high-spin organic species have mainly involved the use of a thermodynamically stable radical, such as triarylmethyl and aminoxyl radicals. For instance, Rajca and co-workers have constructed stable high-spin organic species comprising of triarylmethyls and realized a very high-spin species with values of $S \approx 5000$.[9b] Iwamura and co-workers have used π-conjugated oligo(aminoxyl) radicals as bridging ligands and coordinatively unsaturated paramagnetic 3d transition-metal ions as connectors to construct two and three-dimensional networks in which both the organic 2p and metallic 3d spins have been ordered in macroscopic scales.[10d]

Then, one may ask why one needs to use a persistent triplet carbene as a unit to construct persistent high-spin species. We should emphasize here that the effectiveness of spin source to construct high-spin species should be compared to a system in which a spin unit is incorporated into essentially the same π-networks. It should be noted here that poly(phenylacetylene)s having persistent triplet diarylcarbene units are found to have $S = 9$ spin states,[49] while similar acetylenes having thermodynamically stabilized radicals have been shown to have a spin multiplicity of only 1/2.[50]

Very high-spin organic species comprising of triarylmethyls is achieved by connecting $S = 3$ calix[4]arene macrocycles with $S = 1/2$ bis(biphenylyl)methyl groups, in which out-of-plane twisting, reverting the sign of exchange coupling from ferromagnetic to anti-ferromagnetic, and chemical defects in the interior that interrupt the exchange pathway, have been eliminated, and ferri-magnetic coupling, that is, antiferromagnetic coupling of unequal spins leading to a large net spin magnetic moment, occurs.[9] It may be possible to use persistent triplet carbenes by taking advantage of the stability of our diazo compounds.

We are grateful to our colleagues named in the references and those currently in our group for their time-consuming and pain-taking efforts without which this work would not have been done. We are also grateful to the Ministry of Education, Culture, Sports, Science and Technology of Japan for support of this work through a Grant-in-Aid for Scientific Research for Specially Promoted Research (No. 12002007). The supports from the Mitsubishi Foundation and the Nagase Science and Technology Foundation are appreciated. We also acknowledge Japan Society for the Promotion of Science for an award of a JSPS Fellowship (No P97089) to H. W.

References

1 a) H. Iwamura, *Adv. Phys. Org. Chem.* **1990**, *26*, 179. b) D. A. Dougherty, *Acc. Chem. Res.* **1991**, *24*, 88. c) A. Rajca, *Chem. Rev.* **1994**, *94*, 871. d) T. Takui, *Molecular Magnetism in Organic-Based Materials*, ed. by P. M. Lahti, Marcel Dekker, New York, **1999**. e) *Molecular Magnetism*, ed. by K. Itoh, M. Kinoshita, Kodansha-Gordon and Breach, Tokyo, **2000**.

2 a) O. Kahn, *Molecular Magnetism*, VCH Publishers, Inc. Weinheim, **1993**. b) D. Gatteschi, *Adv. Mater.* **1994**, *6*, 635. c) J. S. Miller, A. J. Epstein, *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 385. d) J. S. Miller, A. J. Epstein, *Chem. Eng. News* **1995**, *73*, 30. e) *Magnetism: A Supramolecular Function*, ed. by O. Kahn, NATO ASI Series C, Kluwer, Dordrecht, **1996**. f) *Molecule-Based Magnetic Materials*, ed. by M. M. Turnbull, T. Sugimoto, L. K. Thompson, ACS Symposium Series 644, American Chemical Society, Washington, **1996**. g) D. Gatteschi, *Curr. Opin. Solid State Mater. Sci.* **1996**, *1*, 192. h) J. S. Miller, A. J. Epstein, *MRS Bull.* **2000**, *25*, 21. i) *Magnetism: Molecules to Materials II*, ed. by J. S. Miller, M. Drillon, Wiley-VCH, **2001**.

3 H. C. Longuet-Higgins, *J. Chem. Phys.* **1950**, *18*, 265.

4 A. A. Ovchinnikov, *Theor. Chim. Acta* **1978**, *47*, 297.

5 W. T. Borden, E. R. Davidson, *J. Am. Chem. Soc.* **1977**, *99*, 4587.

6 a) W. T. Borden, H. Iwamura, J. A. Berson, *Acc. Chem. Res.* **1994**, *27*, 109. b) W. T. Borden, *Diradicals*, ed. by W. T. Borden, Wiley-Interscience, New York, **1982**, pp. 1–12.

7 T. Matsumoto, T. Ishida, N. Koga, H. Iwamura, *J. Am. Chem. Soc.* **1992**, *114*, 9952.

8 a) H. Nishide, T. Kaneko, *Molecular Magnetism in Organic-Based Materials*, ed. by P. M. Lahti, Marcel Dekker, New York, **1999**, pp. 285–303. b) M. Takahashi, S. Yamada, H. Matsuda, H. Nakanishi, E. Tsuchida, H. Nishide, *Chem. Commun.* **1997**, 1853. c) H. Nishide, T. Kaneko, T. Nii, K. Katoh, E. Tsuchida, P. M. Lahti, *J. Am. Chem. Soc.* **1996**, *118*, 9695. d) H. Nishide, K. Maeda, K. Oyaizu, E. Tsuchida, *J. Org. Chem.* **1999**, *64*, 7129. e) H. Nishide, M. Takahashi, J. Takashima, E. Tsuchida, *J. Org. Chem.* **1999**, *64*, 7375.

9 a) A. Rajca, *Molecular Magnetism in Organic-Based Materials*, ed. by P. M. Lahti, Marcel Dekker, New York, **1999**, pp. 345–359. b) A. Rajca, *Chem. Eur. J.* **2002**, *8*, 4835. c) A. Rajca, J. Wongsriratanakul, S. Rajca, *J. Am. Chem. Soc.* **2004**, *126*, 6608. d) A. Rajca, J. Wongsriratanakul, S. Rajca, R. L. Cerny, *Chem. Eur. J.* **2004**, *10*, 3144.

10 a) R.-J. Bushby, *Magnetism: Molecules to Materials II*, ed. by J. S. Miller, M. Drillon, Wiley-VCH, Weinheim, **2001**, pp. 149–187. b) D. B. Amabilino, J. Veciana, *Magnetism: Molecules to Materials II*, ed. by J. S. Miller, M. Drillon, Wiley-VCH, Weinheim, **2001**, pp. 1–60. c) H. Nishide, Y. Hozumi, T. Nii, E. Tsuchida, *Macromolecules* **1997**, *30*, 3986. d) H. Nishide, T. Kaneko, S. Toriu, Y. Kuzumaki, E. Tsuchida, *Bull. Chem. Soc. Jpn.* **1996**, *69*, 499. e) Y. Ishimaru, M. Kitano, H. Kumada, N. Koga, H. Iwamura, *Inorg. Chem.* **1998**, *37*, 2273. f) H. Iwamura, K. Inoue, N. Koga, *New J. Chem.* **1998**, 201. g) P. Rabu, M. Drillon, H. Iwamura, G. Gorlitz, T. Itoh, K. Matsuda, N. Koga, K. Inoue, *Eur. J. Inorg. Chem.* **2000**, 211. h) S. Kanegawa, S. Karasawa, M. Nakano, N. Koga, *Chem. Commun.* **2004**, 1750. i) V. Laukhin, B. Martinez, J. Fontchberta, D. B. Amabilino, M. Minguet, J. Veciana, *J. Phys. Chem.* **2004**, *108*, 18441.

11 a) N. Koga, H. Iwamura, *Carbene Chemistry*, ed. by G. Bertrand, Fontis Media, Lausanne, **2002**, pp. 271–296. b) K. Matsuda, N. Nakamura, K. Takahashi, K. Inoue, N. Koga, H. Iwamura, *Molecule-based Magnetic Materials*, ACS Symposium Series 644, American Chemical Society, Washington, **1996**, p. 142.

12 a) N. Nakamura, K. Inoue, H. Iwamura, T. Fujioka, Y. Sawaki, *J. Am. Chem. Soc.* **1992**, *114*, 1484. b) N. Nakamura, K. Inoue, H. Iwamura, *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 872. c) K. Matsuda, N. Nakamura, K. Takahashi, K. Inoue, N. Koga, H. Iwamura, *J. Am. Chem. Soc.* **1995**, *117*, 5550. d) K. Matsuda, N. Nakamura, K. Inoue, N. Koga, H. Iwamura, *Chem. Eur. J.* **1996**, *2*, 259. e) K. Matsuda, N. Nakamura, K. Inoue, N. Koga, H. Iwamura, *Bull. Chem. Soc. Jpn.* **1996**, *69*, 1483.

13 For reviews of general reactions of carbenes, see: a) W. Kirmse, *Carbene Chemistry*, 2nd ed., Academic Press, New York, **1971**. b) *Carbenes*, ed. by R. A. Moss, M. Jones, Jr., Wiley, New York, **1973** and **1975**, Vols. 1 and 2. c) *Carbene(oide), Carbine*, ed. by M. Regitz, Thieme, Stuttgart, **1989**. d) C. Wentrup, *Reactive Intermediates*, Wiley, New York, **1984**, pp. 162–264.

14 For review of triplet carbenes, see: H. Tomioka, *Reaction Intermediate Chemistry*, ed. by R. A. Moss, M. S. Platz, M. Jones, Jr., Wiley, New York, **2004**, pp. 375–461.

15 a) H. Tomioka, *Acc. Chem. Res.* **1997**, *30*, 315. b) H. Tomioka, *Advances in Carbene Chemistry*, ed. by U. Brinker, JAI Press, Greenwich, CT, **1998**, Vol. 2, pp. 175–214. c) H. Tomioka, *Carbene Chemistry*, ed. by G. Bertrand, Fontis Media S. A., Lansanne, **2002**, pp. 103–152.

16 T. Itoh, Y. Nakata, K. Hirai, H. Tomioka, *J. Am. Chem. Soc.* **2006**, *128*, 957.

17 a) H. Tomioka, E. Iwamoto, H. Itakura, K. Hirai, *Nature* **2001**, *412*, 626. b) E. Iwamoto, K. Hirai, H. Tomioka, *J. Am. Chem. Soc.* **2003**, *125*, 14664.

18 M. Regitz, G. Maas, *Diazo Compounds-Properties and Synthesis*, Academic Press, Orland, **1986**.

19 H. E. Zimmerman, D. H. Paskovich, *J. Am. Chem. Soc.* **1964**, *86*, 2149.

20 K. Sonogashira, *Comprehensive Organic Synthesis*, ed. by B. M. Trost, I. Fleming, Pergamon Press, Oxford, U.K., **1991**, Vol. 3, pp. 521–549.

21 M. R. Doyle, *Reaction Intermediate Chemistry*, ed. by R. A. Moss, M. S. Platz, M. Jones, Jr., Wiley-Interscience, New

Jersey, **2004**, pp. 561–592.

22 T. Iikubo, T. Itoh, K. Hirai, Y. Takahashi, M. Kawano, Y. Ohashi, H. Tomioka, *Eur. J. Org. Chem.* **2004**, 3004.

23 T. K. Dougherty, K. S. Y. Lau, F. L. Hedberg, *J. Org. Chem.* **1983**, *48*, 5273.

24 H. Tomioka, M. Hattori, K. Hirai, K. Sato, D. Shiomi, T. Takui, K. Itoh, *J. Am. Chem. Soc.* **1998**, *120*, 1106.

25 a) K. Sato, D. Shiomi, T. Takui, K. Itoh, T. Kaneko, E. Tsuchida, H. Nishide, *J. Spectrosc. Soc. Jpn.* **1994**, *43*, 280. b) T. Takui, K. Sato, D. Shiomi, K. Itoh, T. Kaneko, E. Tsuchida, H. Nishide, *Magnetism: A Supramolecular Function*, ed. by O. Kahn, Kluwer Academic Publishers, Dordrecht, The Netherlands, **1996**, pp. 249–280.

26 a) M. Yano, K. Sato, D. Shiomi, A. Ichimura, K. Abe, T. Takui, K. Itoh, *Tetrahedron Lett.* **1996**, *37*, 9207. b) K. Sato, M. Yano, M. Furuichi, D. Shiomi, T. Takui, K. Abe, K. Itoh, A. Higuchi, K. Katsuma, Y. Shirota, *J. Am. Chem. Soc.* **1997**, *119*, 6607.

27 J. Isoya, H. Kanda, J. R. Norris, J. Tang, M. K. Bowman, *Phys. Rev. B* **1990**, *41*, 3905.

28 A. V. Astashkin, A. Schweiger, *Chem. Phys. Lett.* **1990**, *174*, 595.

29 T. Takui, Thesis, Osaka University, Osaka, Japan, **1973**.

30 a) J. S. Moore, *Acc. Chem. Res.* **1997**, *30*, 402. b) S. M. Grayson, J. M. Frechet, *Chem. Rev.* **2001**, *101*, 3819.

31 Z. Xu, M. Kahr, K. L. Walker, C. L. Wilkins, J. S. Moore, *J. Am. Chem. Soc.* **1994**, *116*, 4537.

32 T. Itoh, T. Maemura, Y. Ohtsuka, Y. Ikari, H. Wildt, K. Hirai, H. Tomioka, *Eur. J. Org. Chem.* **2004**, 2991.

33 R. L. Carlin, *Magnetochemistry*, Springer-Verlag, Berlin, Germany, **1986**.

34 O. Mongin, C. Papamicaeel, N. Hoyler, A. Gossauer, *J. Org. Chem.* **1998**, *63*, 5568.

35 K. Hirai, E. Kamiya, T. Itoh, H. Tomioka, *Org. Lett.* **2006**, *8*, 1847.

36 B. B. Wright, M. S. Platz, *J. Am. Chem. Soc.* **1983**, *105*, 628; See also: A. M. Trozzolo, R. W. Murray, G. Smolinsky, W. A. Yager, E. Wasserman, *J. Am. Chem. Soc.* **1963**, *85*, 2526; E. Wasserman, R. W. Murray, W. A. Yager, A. M. Trozzolo, G. Smolinsky, *J. Am. Chem. Soc.* **1967**, *89*, 5076; K. Itoh, *Chem. Phys. Lett.* **1967**, *1*, 235.

37 a) D. E. Seeger, J. E. Berson, *J. Am. Chem. Soc.* **1983**, *105*, 5146. b) D. E. Seeger, P. M. Lahti, A. R. Rossi, J. E. Berson, *J. Am. Chem. Soc.* **1986**, *108*, 1251.

38 R. S. Kalgutkar, P. M. Lahti, *J. Am. Chem. Soc.* **1997**, *119*, 4771.

39 For studies of anthrylcarbenes, see: a) E. Wasserman, V. J. Kuck, W. A. Yager, R. S. Hutton, F. D. Greene, V. P. Abegg, N. M. Weinshenker, *J. Am. Chem. Soc.* **1971**, *93*, 6335. b) D. J. Astles, M. Girard, D. Griller, J. Kolt, D. D. M. Wayner, *J. Org. Chem.* **1998**, *53*, 6053.

40 Y. Ohtsuka, T. Itoh, K. Hirai, H. Tomioka, T. Takui, *Org. Lett.* **2004**, *6*, 847.

41 Y. Teki, T. Takui, H. Yagi, K. Itoh, H. Iwamura, *J. Chem. Phys.* **1985**, *83*, 539.

42 Y. Teki, Thesis, Osaka City University, Osaka, Japan, **1985**.

43 For reviews, see for example: a) A. Suzuki, *Metal-Catalyzed Cross-Coupling Reactions*, ed. by F. Diederich, P. J. Stang, Wiley-VCH, Weinheim, **1998**, pp. 49–97. b) S. P. Stanforth, *Tetrahedron* **1998**, *54*, 263. c) N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457.

44 a) H. Tomioka, J. Nakajima, H. Mizuno, E. Iiba, K. Hirai, *Can. J. Chem.* **1999**, *77*, 1066. b) H. Itakura, H. Tomioka, *Org. Lett.* **2000**, *2*, 2995.

45 T. Itoh, K. Hirai, H. Tomioka, *J. Am. Chem. Soc.* **2004**, *126*, 1130.

46 D. Zim, L. Monteiro, J. Dupont, *Tetrahedron Lett.* **2004**, *41*, 8199.

47 T. Masuda, T. Yoshimura, J. Fujimori, T. Higashimura, *J. Chem. Soc., Chem. Commun.* **1987**, 1805.

48 Y. Kishimoto, P. Eckerle, T. Miyatake, M. Kainosho, A. Ono, T. Ikariya, R. Noyori, *J. Am. Chem. Soc.* **1999**, *121*, 12035, and references therein.

49 T. Itoh, Y. Jinbo, K. Hirai, H. Tomioka, *J. Am. Chem. Soc.* **2005**, *127*, 1650.

50 a) Y. Miura, M. Matsumoto, Y. Ushitani, Y. Taki, T. Takui, K. Itoh, *Macromolecules* **1993**, *26*, 6673. b) H. Nishide, T. Kaneko, M. Igarashi, E. Tsuchida, N. Yoshioka, P. M. Lathi, *Macromolecules* **1994**, *27*, 3082. c) P. M. Lahti, A. L. Inceli, F. C. Rossitto, *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 2167.

51 a) N. Koga, H. Iwamura, *Molecular Magnetism in Organic-Based Materials*, ed. by P. M. Lahti, Marcel Dekker, New York, **1999**, pp. 629–659. b) N. Koga, H. Iwamura, *Mol. Cryst. Liq. Cryst.* **1997**, *305*, 415. c) H. Iwamura, N. Koga, *Mol. Cryst. Liq. Cryst.* **1999**, *334*, 437. d) H. Iwamura, N. Koga, *Pure Appl. Chem.* **1999**, *71*, 231.

52 a) Y. Sano, M. Tanaka, N. Koga, K. Matsuda, H. Iwamura, P. Rabu, M. Drillon, *J. Am. Chem. Soc.* **1997**, *119*, 8246. b) S. Karasawa, N. Koga, *Polyhedron* **2001**, *20*, 1387. c) S. Karasawa, Y. Sano, T. Akita, N. Koga, T. Itoh, H. Iwamura, P. Rabu, M. Drillon, *J. Am. Chem. Soc.* **1998**, *120*, 10080. d) S. Karasawa, H. Kumada, N. Koga, H. Iwamura, *J. Am. Chem. Soc.* **2001**, *123*, 9685. e) H. Morikawa, F. Imamura, Y. Tsurukami, T. Itoh, H. Kumada, S. Karasawa, N. Koga, H. Iwamura, *J. Mater. Chem.* **2001**, *11*, 493. f) S. Karasawa, N. Koga, *Polyhedron* **2003**, *22*, 1877.

53 a) J.-M. Lehn, *Supramolecular Chemistry*, VCH Publisher, **1995**. b) J.-F. Nierengarten, C. O. Dietrich-Buchecker, J.-P. Sauvage, *J. Am. Chem. Soc.* **1994**, *116*, 375. c) J.-F. Leininger, B. Olenyuk, P. J. Stang, *Chem. Rev.* **2000**, *100*, 853.

54 a) H. Tomioka, T. Watanabe, K. Hirai, K. Furukawa, T. Takui, K. Itoh, *J. Am. Chem. Soc.* **1995**, *117*, 6376. b) H. Tomioka, M. Hattori, K. Hirai, *J. Am. Chem. Soc.* **1996**, *118*, 8723. c) H. Tomioka, T. Watanabe, M. Hattori, N. Nomura, K. Hirai, *J. Am. Chem. Soc.* **2002**, *124*, 474. d) K. D. Karlin, T. Iikubo, H. Tomioka, *Chem. Lett.* **2004**, *33*, 1226.

55 M. Matsuno, T. Itoh, K. Hirai, H. Tomioka, *J. Org. Chem.* **2005**, *70*, 7054.

56 Y. Sugiura, *Inorg. Chem.* **1978**, *17*, 2178.

57 T. Itoh, M. Matsuno, S. Ozaki, K. Hirai, H. Tomioka, *J. Phys. Chem. B* **2005**, *109*, 20763.

58 N. Mataga, *Theor. Chim. Acta* **1968**, *10*, 1509.

59 a) A. Rajca, S. Rajca, J. Wongsriatanakul, *J. Am. Chem. Soc.* **1999**, *121*, 6308. b) A. Rajca, J. Wongsriatanakul, S. Rajca, *Science* **2001**, *294*, 1503. c) K. K. Anderson, D. A. Dougherty, *Adv. Mater.* **1998**, *10*, 688. d) R. J. Bushby, D. R. McGill, K. M. Ng, N. Taylor, *J. Mater. Chem.* **1997**, *7*, 2343. e) H. Nishide, T. Ozawa, M. Miyasaka, E. Tsuchida, *J. Am. Chem. Soc.* **2001**, *123*, 5942.

60 T. Itoh, M. Matsuno, E. Kamiya, K. Hirai, H. Tomioka, *J. Am. Chem. Soc.* **2005**, *127*, 7078.

Tetsuji Itoh was born in Mie in 1967. He received M.S. degree in 1992 from Mie University, and the Ph.D. degree in 1996, from the Graduate University for Advanced Studies under the supervision of Prof. Kazuhiro Nakasuji. He worked with Prof. Hiizu Iwamura and Noboru Koga at Kyushu University as Postdoctoral Fellow in 1996–2001. He joined Professor Tomioka's group at Department of Chemistry for Materials, Faculty of Engineering of Mie University in 2001 as a Researcher. His research interests are structural and physical organic chemistry, mainly the construction of molecule-based magnets using triplet carbene units.

Katsuyuki Hirai was born in Mie in 1963. He received M.S. degree in 1986 from Mie University and Ph.D. degree in 1997 from Nagoya University. He was appointed as Research Assistant in 1986 at the Faculty of Engineering, Mie University and was promoted to Assistant Professor in the Instrumental Analysis Center, Mie University in April, 1999. He is Assistant Professor in the Life Science Research Center, Mie University since 2003. His current research interests are isolation of triplet carbene and the construction of organo magnetic materials.

Hideo Tomioka received M.S. and Ph.D. degrees in 1966 and 1969, respectively, from Nagoya University under the direction of Prof. Yoshiro Ogata and Yasuji Izawa. He was appointed as Associate Professor in 1971 and promoted to Professor in 1985 at the Faculty of Engineering, Mie University where he has been an Emeritus Professor since 2005. He has also been Visiting Professor at Aichi Institute of Technology since 2005. His current interests include the study of neutral reactive species using spectroscopic and computational techniques coupled with traditional product analysis methods. He received the Japanese Photochemistry Award in 1991 and the Divisional Award of the Chemical Society of Japan on 1997.