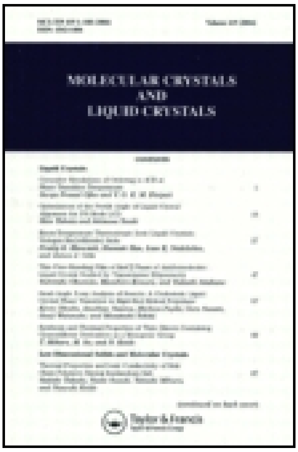

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Electronic and Molecular Structures of Dendrimeric High-spin Polycarbenes as Studied by CW and Pulsed ESR-based Electron Spin Transient Nutation Spectroscopy

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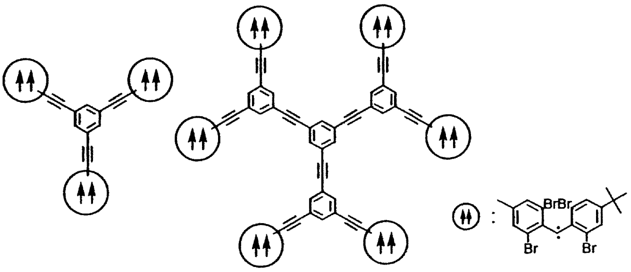
Abstract: Highly symmetric high-spin polycarbenes of π-conjugation, which are the first and second generations of the spin-mediated dendrimers based on phenylacetylenes, have been studied by cw and pulsed ESR spectroscopy. We measured pulsed ESR-based two-dimensional electron-spin transient nutation (2D-ESTN) spectra of the stabilized polycarbene systems connecting the phenylacetylene moieties at the meta-positions of benzene rings, and we determined their spin multiplicity with the help of a transition moment analysis. A septet ground state of the triscarbene system, which is the first generation of the phenylacetylene dendrimers, was unequivocally discriminated. It is indicated that the stable diphenylcarbene serves as a useful building block and the phenylacetylene dendrimer as a ferromagnetic coupling unit with robust spin polarization for super high-spin polymeric systems and super paramagnetic materials.

Keywords organic high-spin molecule; high-spin polycarbene; phenylacetylene dendrimer; pulsed ESR; electron spin transient nutation

INTRODUCTION

Organic molecular magnetic materials have been attracting continuous interest in the pure and applied sciences. We have developed organic high-spin systems using topological nature in π-conjugation systems and identified their molecular spin multiplicity by invoking an electron spin transient nutation (ESTN) method[1-3] based on pulsed ESR spectroscopy. The topological nature in the π-conjugation system has been well-established in the field of purely organic magnetics so far. We designed highly symmetric high-spin polycarbene systems using persistent polybrominated diphenylcarbenes as spin units and phenylacetylene dendrimers as spin coupling units in order to construct purely organic molecule-based super high-spin systems/super paramagnetic materials. The polybrominated diphenylcarbene has been developed by Tomioka *et al.* and known as a persistent triplet carbene in solid[4]. The persistent carbene is applicable as spin units for constructing the high-spin molecules with less reactivity. On the other hand, a series of the phenylacetylene dendrimers with well-controlled structures have been attracting much attention as good candidates for artificial antennae exhibiting light harvesting property[5-7]. The dendrimers connecting the phenylacetylene moieties at the *meta*-positions of benzene rings are expected to be topologically controlled ferromagnetic couplers. The designed tris- and hexakis-carbene systems with dendrimeric structures are shown in Figure 1. They are the first and second generations of the spin-mediated dendrimers composed of the phenylacetylene molecules. When dynamic spin polarization mechanism dominates in the π-conjugation system, both the dendrimeric structures in Figure 1 are expected to be ground-state septet (S=3) for **1** and ground-state tridecet (S=6) for **2**, in which the triplet spin units ferromagnetically



1 **2**

FIGURE 1 Dendrimeric high-spin polycarbene systems based on the phenylacetylene dendrimers interact with each other due to the topological symmetry requirement. In order to study the electronic structures of the polycarbene systems and characteristics of the phenylacetylene dendrimer as the spin linkers, we have applied powder-pattern cw-ESR and two-dimensional ESTN spectroscopy to the high-spin polycarbene systems with the dendrimeric structures. Naturally, high-spin molecular systems with both extremely high spins and highly symmetric molecular structures are challenging targets in terms of spectroscopy for unequivocal spin-multiplicity identification. The 2D-ESTN method is capable of discriminating high-spin species by differences in the transition moment. The 2D-ESTN spectroscopy is classified as a new type of spectroscopy termed transition moment spectroscopy. In this paper, we report spin identifications of the dendrimeric high-spin polycarbenes by the 2D-ESTN spectroscopy and their molecular and electronic structures. We discuss the feasibility of constructing super high-spin polymeric systems/super paramagnetic materials composed of the polycarbenes under study.

EXPERIMENTAL

The polycarbenes were generated in a 2-methyltetrahydrofuran (2-MTHF) organic glass at liquid helium temperature by irradiation of the corresponding diazo precursors with a SAN-EI UVF-351S 300W high-pressure mercury lamp. X-band cw and pulsed ESR measurements were carried out on Bruker ESP300 and 380 spectrometers with a dielectric resonator and a 1kW TWT amplifier, respectively. The ESTN experiments were performed by monitoring the peak of a 2-pulse Hahn echo after a microwave excitation pulse with different pulse length (t_1). We constructed field-swept 2D-ESTN spectra by sweeping the static magnetic field. The nutation frequency ω_n for an $|S, M_S> \leftrightarrow |S, M_S + 1>$ ESR allowed transition, which is proportional to a transition moment to the first order, is given by

$$\omega_n = \sqrt{S(S+1) - M_S(M_S+1)} \times \omega_1 \qquad (1)$$

in the weak extreme limit of the microwave irradiation ($\omega_1 << \omega_D$ where ω_D is a fine structure coupling in the frequency unit). ω_l ($\approx \gamma B_l$) corresponds to the strength of the microwave irradiation field.

RESULTS AND DISCUSSION

Triscarbene System 1

A fine-structure ESR spectrum observed after the UV irradiation of the corresponding diazo precursor of **1** indicates broad absorption lines in a wide range from 0.1 to 0.6 T. Salient features of organic high-spin molecules apparently failed to show up in the observed spectrum. Canonical peaks dominated in the g~2 region and key-peaks appearing in the wings away from the g~2 region were only vague. From the field-swept 2D-ESTN spectra of **1** observed at 5K, three dominant peaks were discriminated. The ratio of the observed nutation frequencies agrees well with the theoretical one of $\sqrt{6}:\sqrt{10}:2\sqrt{3}$ expected for $|S=3, M_S=\pm3> \leftrightarrow |3,\pm2>$, $|3,\pm2> \leftrightarrow |3,\pm1>$, and $|3,\pm1> \leftrightarrow |3{,}0>$ transitions in a septet state by eq.(1). Up to 90K from 2.6K, no other nutation peaks attributable to lower spin states ($S\geq1$) were observed, showing the septet state to be the ground state of **1** with the excited low-spin states located above 300 cm^{-1}.

A nutation peak arising from any doublet species of by-products was not detected in the whole ESTN measurements, showing a remarkable chemical stability of **1**. A thermal stability of **1** also manifested itself during an annealing process. A significant change in the ESR signal shape was observed when the matrix temperature was raised above 140K and kept for 15min. New fine-structure signals were irreversible with temperature. In the ESR spectrum of **1** observed at 3.1K after the annealing process, fine-structure parameters of the annealed **1** were determined by a spectral simulation. The spectral simulation was numerically carried out using the eigenfield method[8]. The best-fit spin-Hamiltonian parameters are $S = 3$, $g = 2.003$ (isotropic), $D = -0.040$ cm^{-1}, and $|E| = 0.007$ cm^{-1}. The experimentally obtained fine-structure parameters for **1** before annealing were close to those after annealing but erroneous because of the line broadening. The broadening is presumably due to statistical fluctuation of molecular conformations of the diphenylcarbenes around the cylindrical triple-bond axis of the ethynyl group.

A semiempirical calculation for the fine-structure parameters of **1** using those of the triplet spin unit was made in order to discuss the electronic and molecular structures of **1**. The negative D and non-vanishing E values were understood to be due to subtle departure from the C_3 symmetry of the molecular structure by rotation of the diphenylcabenes around the ethynyl groups. The calculated value was in agreement with the experimental one, indicating that the three carbene units are interacting ferromagnetically with each other in the septet state of **1**. The $|E|$ value calculated with the asymmetrical rotation of the diphenylcarbene moieties, however, was underestimated. Recently Bochkarev *et al.* have reported an unusual non-planar molecular structure of 1,3,5-tris(phenylethynyl)benzene in terms of X-ray crystallography[9]. Such a non-planer structure in the dendrimer skeleton that a phenylacetylene moiety is perpendicular to the others gives a large E value rather than the molecular structure with the asymmetrical information of the three diphenylcarbene moieties, being consistent with the experimental $|E|$ value.

Hexakiscarbene System **2**

A fine-structure ESR spectrum of a high-spin molecule generated by the UV irradiation of the hexadiazo precursor was observed. It was difficult to identify a spin state of the generated high-spin molecule because of the broad fine-structure spectrum without the fingerprints characterizing the spin state. Figure 2 shows a contour plot of the 2D-ESTN spectra of the photolyzed precursor observed at 3.5K. The highest frequency which was 4.7 times greater than ω_1 was observed at the magnetic field around 0.35 T. Considering the relative ratio of ω_n/ω_1 calculated by eq.(1), the nutation frequencies designated by a, b, c, and d were attributed to $|4,\pm4> \leftrightarrow |4,\pm3>$, $|4,\pm3> \leftrightarrow |4,\pm2>$, $|4,\pm2> \leftrightarrow |4,\pm1>$, and $|4,\pm1> \leftrightarrow |4,0>$ ESR allowed transitions of the nonet state (S=4), respectively. Distinct nutation frequencies due to the expected tridecet state (S=6) were not identified. Magnetization measurements on the generated high-spin molecule, which indicate a magnetization curve due

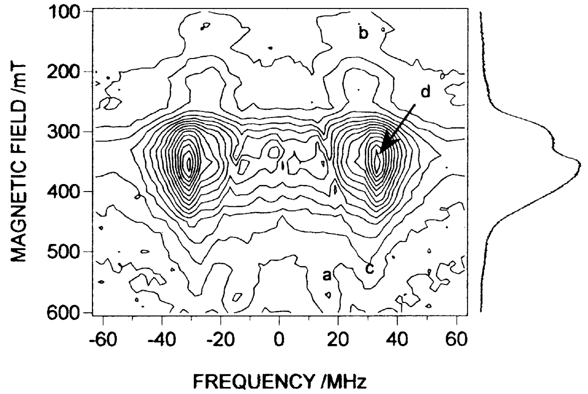


FIGURE 2 2D-ESTN spectrum of the hexakiscarbene **2**.

to the high-spin molecule with an effective spin quantum number less than *S*=6, are consistent with the result of the 2D-ESTN experiments. Iwamura *et al.* have reported the disturbance to generate expected high-spin states by an intramolecular coupling between the divalent carbon atoms in polycarbene systems[10]. Such intramolecular reaction is not expected in the present stable polybrominated diphenylcarbene due to less reactivity of the divalent carbon atoms protected by the bromine atoms. We concluded that the nonet state was attributed to a partially photolyzed product generated under the present experimental condition. More elaborate conditions for UV photolysis are under examination.

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