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Room-Temperature High-Spin Organic Single Molecule: Nanometer-Sized and Hyperbranched Poly[1,2,(4)-phenylenevinyleneanisylaminium]

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Abstract: Poly[1,2,(4)-phenylenevinyleneanisylaminium] **1** was synthesized by one-pot palladium-catalyzed polycondensation of *N*-(3-bromo-4-vinylphenyl)-*N*-(4-methoxyphenyl)-*N*-(4-vinylphenyl)amine **3** and subsequent oxidation with the thianthrene cation radical tetrafluoroborate: compound **1** three-directionally satisfies a non-Kekulé-type π-conjugation and the ferromagnetic connectivity of the unpaired electrons of the triarylaminium cationic radical. The average molecular weight of the polymer was 4700−5900 (degree of polymerization = 11−14), which gave a single molecular-based and globular-shaped image of ca. 15 nm diameter by atomic and magnetic force microscopies under ambient conditions. The aminium polyradical **1** with a spin concentration (determined by iodometry) of 0.65 spin/unit displayed an average *S* (spin quantum number) value of $^{7}/_{2}$ even at 70 °C according to NMR and magnetization measurements.

Introduction

Due to the possibility of obtaining purely organic-derived magnetic materials, there has been current interest in the synthesis of very high-spin polyradical molecules based on a ferromagnetic spin alignment through the π-conjugated skeleton of a molecule.[1] These high-spin molecules are designed to satisfy a π-conjugated but non-Kekulé and nondisjoint connectivity[2] among the nonbonding molecular orbitals of the unpaired electrons.[3,4] Along with this molecular designing, they have been extended to cross-linked or networked π-conjugation systems.[3a,4a] Rajca et al.[5] eventually synthesized two-dimensionally dendritic macrocyclic poly(1,3-phenylenephenylmethine)s with magnetic ordering and a huge magnetic moment corresponding to *S* (spin quantum number) > 5000. However, the triarylmethane radical survives only below 200 K. Chemically stable radical species are desired in such a network high-spin polyradical to raise the temperature range of magnetic ordering and possibly provide a molecular-based purely organic magnetic material.

On the other hand, we have recently succeeded in applying magnetic force microscopy (MFM) to effectively study the molecular image and very weak magnetic response of an organic radical macromolecule with molecular size from 10 to 1000 nm.[6] The MFM images of the magnetic particles showed a magnetic gradient response with a fairly high resolution on a 10 nm scale at the position of the radical molecule dispersed on a substrate surface at room temperature. The MFM molecular image has been examined as a magnetic dot, by use of organic radical samples with different molecular weights and spin concentrations.[6b] However, the magnetic response upon MFM was also ascribed to paramagnetic radical macromolecules,[7] and there still remains the pending subject of a nanometer-scale study on a high-spin organic molecule under ambient conditions. From such a viewpoint, one of the unrealized benchmarks for exploring a single molecular-based and purely organic magnetism is to synthesize a practically available high-spin organic molecule with good stability under ambient conditions.

While a number of the ground-state high-spin organic radical molecules synthesized along the molecular designing of non-Kekulé and nondisjoint fashion are known, as far as we know, only a few of these radical molecules, such as the tri(chlorophenyl)methyl radical synthesized by Veciana et al.[8] and the triplet Yang's biradical,[9] display high-spin magnetic pa-

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(1) (a) *Magnetic Properties of Organic Materials*; Lahti, P. M., Ed.; Marcel Dekker: New York, 1999. (b) *π-Electron Magnetism From Molecules to Magnetic Materials*; Veciana, J., Ed.; Springer: Berlin, 2001. (c) Rajca, A. *Chem. Eur. J.* **2002**, *8*, 4834. (d) Baumgarten, M. In *Progress in Theoretical Chemistry and Physics*; Lund, A., Shiotani, M., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2003; Vol. 10, Chapt. 12. (e) Rajca, A. *Adv. Phys. Org. Chem.* **2005**, *40*, 153.

(2) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587.

(3) (a) Rajca, A.; Rajca, S.; Wongsriratanakul, J. *J. Am. Chem. Soc.* **1999**, *121*, 6308. (b) Teki, Y.; Miyamoto, S.; Nakatsuji, M.; Miura, Y. *J. Am. Chem. Soc.* **2001**, *123*, 294. (c) Nishide, H.; Nambo, M.; Miyasaka, M. *J. Mater. Chem.* **2002**, *12*, 3578. (d) Kaneko, T.; Makino, T.; Miyaji, H.; Teraguchi, M.; Aoki, T.; Miyasaka, M.; Nishide, H. *J. Am. Chem. Soc.* **2003**, *125*, 3554. (e) Rajca, A.; Wongsriratanakul, J.; Rajca, S. *J. Am. Chem. Soc.* **2004**, *126*, 6608. (f) Rajca, A.; Wongsriratanakul, J.; Rajca, S.; Cerny, R. L. *Chem. Eur. J.* **2004**, *10*, 3144. (g) Fukuzaki, E.; Takahashi, N.; Imai, S.; Nishide, H.; Rajca, A. *Polym. J.* **2005**, *37*, 284. (h) Rajca, A.; Shiraishi, K.; Vale, M.; Han, H.; Rajca, S. *J. Am. Chem. Soc.* **2005**, *127*, 9014.

(4) (a) Bushby, R. J.; Gooding, D. *J. Chem. Soc., Perkin Trans. 2*. **1998**, 1069. (b) Selby, T. D.; Blackstock, S. C. *Org. Lett.* **1999**, *1*, 2053. (c) van Meurs, P. J.; Janssen, R. A. J. *J. Org. Chem.* **2000**, *65*, 5712. (d) Murata, H.; Takahashi, M.; Namba, K.; Takahashi, N.; Nishide, H. *J. Org. Chem.* **2004**. *69*. 631.

(5) Rajca, A.; Wongsriratanakul, J.; Rajca, S. *Science* **2001**, *294*, 1503.

(6) (a) Nishide, H.; Ozawa, T.; Miyasaka, M.; Tsuchida, E. *J. Am. Chem. Soc.* **2001**, *123*, 5942. (b) Miyasaka, M.; Saito, Y.; Nishide, H. *Adv. Funct. Mater.* **2003**, *13*, 113.

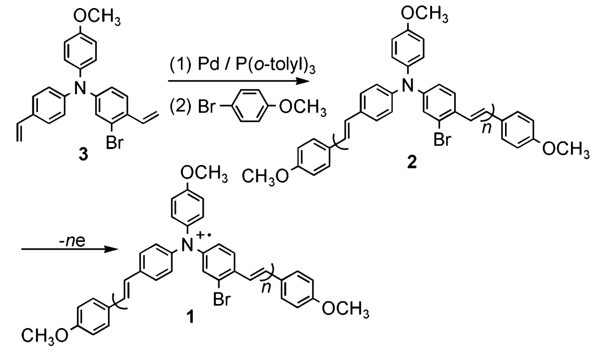
(7) Michinobu, T.; Inui, J.; Nishide, H. *Polym. J.* **2003**, *35*, 71.

(8) Veciana, J.; Rovira, C.; Ventosa, N.; Crespo, M. I.; Palacio, F. *J. Am. Chem. Soc.* **1993**, *115*, 57.

(9) (a) Yang, N. C.; Castro, A. J. *J. Am. Chem. Soc.* **1960**, *82*, 6208. (b) Mukai, K.; Ishizu, K.; Deguchi, Y. *J. Phys. Soc. Jpn.* **1969**, *27*, 783.

10.1021/ja0569611 CCC: $33.50

Scheme 1



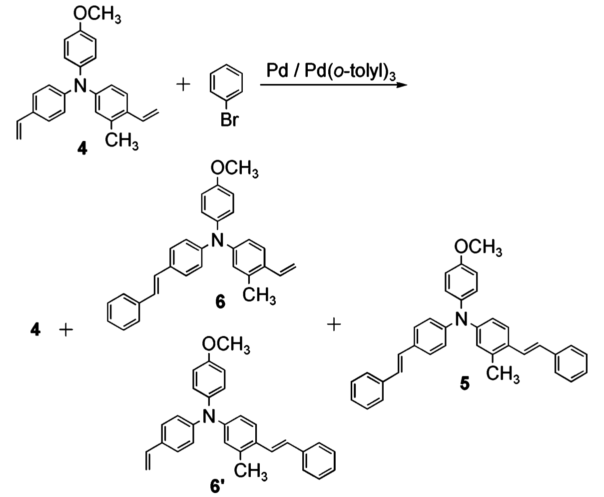
rameters at high temperatures such as room temperature. The radical species involved in these molecules possess a tradeoff relation between sufficient exchange interaction for spin alignment and chemical stability. Among the list of radical species, the triarylaminium radical is a favorable candidate for the spin source to be utilized in robust high-spin purural-radical molecules at room temperature. From such a viewpoint, a series of aminium polyradicals has been synthesized and their magnetic behaviors have been reported. However, they often lacked solvent solubility that lead to both a limitation of radical (spin) generation yield and a lack of chemical structure identification. To the best of our knowledge, no high-spin molecules at room temperature have been studied by use of aminium radical polymers with well-defined chemical structure.

This paper describes the first example of room-temperature high-spin purely organic molecules possessing a nanometer-range single molecular size. The high-spin molecule poly[1,2,-(4)-phenylenevinyleneanysilaminium] **1** was designed to be hyperbranched in a π-conjugated but non-Kekulé and nondisjoint fashion. The aminium polyradical **1** was synthesized via the one-pot polycondensation of an asymmetric trifunctional monomer **3** and subsequent careful oxidation. Compound **1** was soluble in common solvents and durable under ambient conditions. The single molecular-based high-spin behavior of **1** was examined by NMR and magnetization measurements and magnetic force microscopy at room temperature.

Results and Discussion

The hyperbranched and head-to-tail linked poly(phenylenevinylene), poly[1,2,(4)-phenylenevinyleneanisylamine] **2**, was synthesized via one-pot palladium-catalyzed[10] polycondensation of an asymmetric trifunctional (the bromo, two kinds of vinyl groups) monomer, *N*-(3-bromo-4-vinylphenyl)-*N*-(4-methoxyphenyl)-*N*-(4-vinylphenyl)amine **3**, which was prepared by coupling 4-[*N*-(4-methoxyphenyl)amino]benzaldehyde and 2-bromo-4-iodobenzaldehyde and the following Wittig reaction (Scheme 1). A gel-permeation chromatographic (GPC) profile of the polymer (uncapped) **2** was unimodal. Bromine was detected at less than 2 wt % in the elemental analysis. Further reaction of the isolated polymer by the Pd catalyst resulted in recovery of the starting polymer. These results denied a coupling reaction between the oligomers during the polymerization because the surface of the oligomer and polymer is occupied by the vinyl groups of the monomer. The hyperbranched and head-to-tail structure was characterized by ^{1}H NMR, UV/vis, and fluorescence spectroscopies. For example, the NMR integration ratio of two vinyl groups was almost unity, indicating a highly branched polymer structure. The end vinyl groups of the polymer were capped by reaction with excess *p*-bromoanisole to give **2**, to avoid all side reactions of the vinyl groups in the following radical generation.

Scheme 2



The head-to-tail linkage and the branched structure were further supported by the model reaction of *N*-(4-methoxyphenyl)-*N*-(3-methyl-4-vinylphenyl)-*N*-(4-vinylphenyl)amine **4** and *p*-bromobenzene by use of the same Pd catalyst and condensation reaction conditions; the model reaction represented in Scheme 2 gave *N*-(4-methoxyphenyl)-*N*-(3-methyl-4-styrylphenyl)-*N*-(4-styrylphenyl)amine **5** (for details, see the Experimental Section). The branched structure and the degree of branching[11] were examined on the basis of the NMR integral ratios of the vinyl and methoxy groups of the terminal unit **4**, the linear units **6** and **6′**, and the dendritic unit **5**. The branching unit **5** was predominantly favored in comparison with the linear **6** and **6′** unit formation.[12] The degree of branching for the model reaction was ca. 0.5. These results indicated that poly[1,2,(4)-phenylenevinyleneanisylamine] **2** with a highly branched structure was formed under these experimental conditions (Figure 1).

The UV/vis absorption and fluorescence of the hyperbranched polymer **2** ($\lambda_{max} = 300$, 385 nm and $\lambda_{em} = 505$ nm, respectively) were comparable with those for the linear corresponding polymer poly{4-[bis(4-methoxyphenyl)amino]-1,2-phenylenevi-

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[10] Heck, R. F. *Org. React.* **1982**, *27*, 345.

[11] (a) Thompson, D. S.; Markoski, L. J.; Moore, J. S. *Macromolecules* **1999**, *32*, 4764. (b) *Dendrimers and Other Dendritic Polymers*; Fréchet, J. M. J.; Tomalia, D. A., Eds.; John Wiley & Sons: Chichester, U.K., 2001. (c) Jikei, M.; Kakimoto, M. *Prog. Polym. Sci.* **2001**, *26*, 1233.

[12] NMR spectrum of the reaction mixture showed multiple peaks at 5.7−5.1 and 3.8 ppm, which were ascribed to the vinyl and methoxy groups of the compounds formed in the model reaction. Each peak was attributed to the terminal unit **4**, the linear units **6** and **6′**, and the dendritic unit, *N*-(4-methoxyphenyl)-*N*-(3-methyl-4-styrylphenyl)-*N*-(4-styrylphenyl)-amine **5**, by the following HPLC separation, and mass, and ^{1}H NMR spectroscopies. The ratio of the vinyl groups [linear (L)/terminal (T) = 2.02/1] and the ratio of the methoxy groups [dendritic (D)/L/T = 0.91/2.08/1] in the NMR spectrum gave the degree of branching [= (D + T)/(L + D + T) = 2T/(L + 2T)] for the products of the model reaction to be 0.50 and 0.48, respectively. *N*-(4-Methoxyphenyl)-*N*-(3-methyl-4-styrylphenyl)-*N*-(4-styrylphenyl)amine **5**: IR (KBr pellet) 2932 ($\nu_{Ar\ C-H}$), 1241 (ν_{C-O-C}), 961 cm^{-1} ($\delta_{Ar\ C-H}$); ^{1}H NMR (CDCl$_3$, 500 MHz) $\delta = 7.51-6.85$ (m, 13H, aryl), 7.38 (d, $J = 8.4$ Hz, 2H, aryl), 7.31 (d, $J = 18$ Hz, 1H, vinylene), 7.25 (d, $J = 19$ Hz, 1H, vinylene), 7.10 (d, $J = 8.8$ Hz, 2H, aryl), 7.03(2) (d, $J = 19$ Hz, 1H, vinylene), 7.02(7) (d, $J = 8.4$ Hz, 2H, aryl), 6.90 (d, $J = 18$ Hz, 1H, vinylene), 3.82 (s, 3H, methoxy), 2.33 (s, 3H, methyl); mass calcd for M 493.6, found (*m*/*z*) 494 (M$^+$). For **6** and **6′**, see Supporting Information.

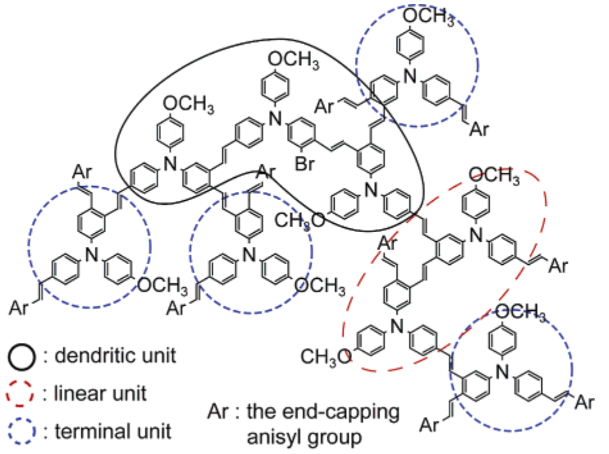

Figure 1. Structure of the hyperbranched poly(1,2,(4)-phenylenevinyleneanisylamine) **2**.

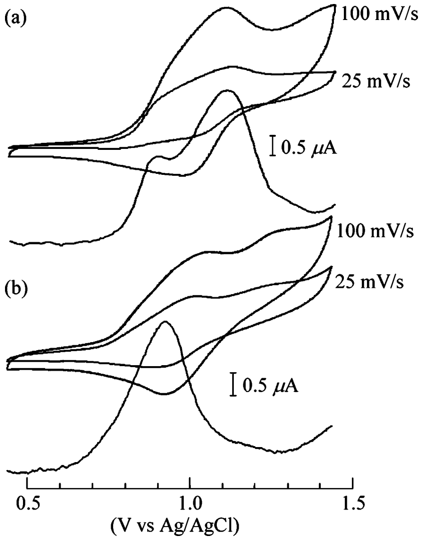

Figure 2. Cyclic and differential pulse voltammograms of **2** with DP = 12 (a) and DP = 4 (b) in CH_2Cl_2 with 0.1 M $(C_4H_9)_4NBF_4$.

nylene} (λ_{max} = 302, 368 nm and λ_{em} = 528 nm), which suggested a developed π-conjugation in **2**. The molecular weight of **2** was, for example, 5200 [degree of polymerization (DP) = 12]. Compound **2** was a yellow powder and quite soluble in the common solvents such as benzene, $CHCl_3$, and tetrahydrofuran (THF). The solution viscosity of **2** (DP = 12) was 1 order of magnitude lower (intrinsic solution viscosity [η] = 0.014 g/dL) than that of the corresponding linear polymer (DP = 13, [η] = 0.12 g/dL). An extremely low solution viscosity is one of the characteristics of hyperbranched polymers, which is ascribed to the highly branched and globular structure.

Cyclic voltammetry of **2** showed a redox wave with the oxidation peak at 1.0 V vs Ag/AgCl and the redox peak separation of 120 mV at a sweep rate of 100 mV s^{-1} (Figure 2): The voltammogram was repeatedly recorded for potential sweeps of 100 times at room temperature. The electrolytic electron spin resonance (ESR) spectrum was recorded under the potential at 1.2 V. A strong absorption appeared at g = 2.0028, indicating a nitrogen-centered radical generation. The ESR absorption disappeared under the potential at 0.6 V. These results mean that the triarylamine moiety is electrochemically oxidized to the triarylaminium cationic radical and reversibly reduced to the starting amine and that the aminium radical is chemically persistent even in a solution at room temperature without any subsequent chemical side reactions. The differential pulse voltammogram displayed two oxidation peaks at 0.9 and 1.1 V. The cyclic voltammetry of **2** at the slow scan rate of 25 mV s^{-1} also showed a new redox wave at ca. 0.9 V or a two-stepped quasi-reversible wave. On the other hand, the cyclic voltammogram for **2** with the lower molecular weight of 1700 (degree of polymerization = 4) (Figure 2b) showed a unimodal oxidation wave at 0.9 V. These results suggest that the oxidation of the amine moiety or the cationic radical generation inside the hyperbranched polymer **2** is kinetically shielded by the outer layer and that the oxidation potential for the dendritic amine moiety inside the polymer is lower (0.9 V) than that (1.1 V) for the terminal amine moiety.[13]

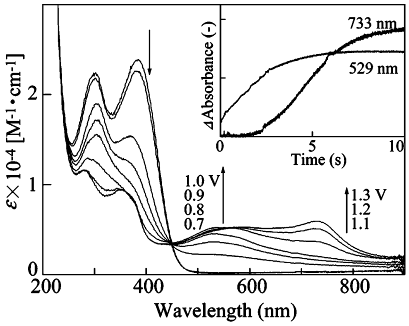

Figure 3. Electrolytic UV/vis spectrum of the CH_2Cl_2 solution of the hyperbranched polymer **2** (DP = 12) with 0.1 M $(C_4H_9)_4NBF_4$ under the given potential. Inset: Absorption change of the CH_2Cl_2 solution of 0.1 mM **2** after mixing with the CH_2Cl_2 solution of 2 mM $NOSbF_6$.

The CH_2Cl_2 solution of the hyperbranched polymer **2** was electrochemically oxidized under the given potential up to 1.3 V and the UV/vis spectrum was recorded. An absorption peak appeared at λ_{max} = 529 nm with an isosbestic point at 447 nm in the range of 0.7−1.0 V and a new peak occurred at λ_{max} = 733 nm with an isosbestic point at 565 nm at greater than 1.0 V. This result indicated that the hyperbranched polymer **2** possesses two amine moieties oxidized at each potential, 0.8−1.0 and 1.1−1.3 V, and these two amine moieties were oxidized to two aminium radicals with visible absorption maxima at 529 and 733 nm.

The hyperbranched polymer **2** was oxidized with nitrosonium hexafluoroantimonate ($NOSbF_6$) in a stopped-flow UV/vis spectrophotometer (inset of Figure 3). $NOSbF_6$ was selected as the oxidizing agent because it has no absorption in the UV/vis region and a bulky counteranion, SbF_6^-, to stabilize the formed aminium cation radical. After the oxidation of the inside and dendritic amine moiety with the lower oxidation potential, the oxidation of the amine moiety located on the outside of the polymer with the higher potential was observed with the absorbance increase at 733 nm.

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(13) The basicity gradient and the metal complexation rate of the amine moieties for the dendritic poly(phenylazomethine)s suggested the following two features of the dendritic and hyperbranched aromatic polymers: (a) Yamamoto, K.; Higuchi, M.; Shiki, S.; Tsuruta, M.; Chiba, H. *Nature* **2002**, *415*, 509. (b) Satoh, N.; Nakashima, T.; Yamamoto, K. *J. Am. Chem. Soc.* **2005**, *127*, 13030. (i) The basicity of the amine moieties inside the polymer is higher than that outside, because a Coulombic repulsion among the sterically crowded amine moieties outside the polymer retards the aminium cation formation. (ii) The reaction on the amine moieties inside the polymer is slower than that outside due to a steric shielding with the outer shell. These could be also the case for the oxidation of the hyperbranched polymer **2**. The corresponding linear-type poly(4-dianisylamino-1,2-phenylenevinylene) showed a unimodal oxidation wave during cyclic voltammetry even at a slow scan rate and the relatively low oxidation potential of 0.81 V vs Ag/AgCl.[4d]

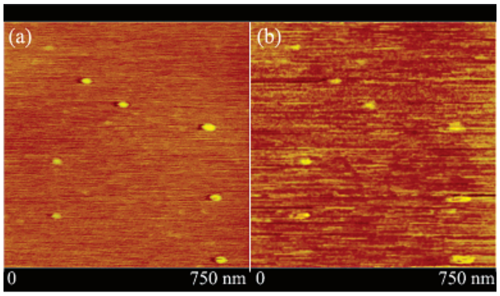

Figure 4. AFM (tapping mode) image (a) and MFM (noncontact mode) image (b) of the polyradical **1** with DP = 12 at room temperature.

The hyperbranched polymer **2** was also chemically converted to the aminium polyradical **1** with an equivalent amount of thianthrene radical tetrafluoroborate[14] in an acidic solvent (CH_2Cl_2/trifluoroacetic acid/trifluoroacetic anhydride = 81/17/2 v/v/v).[15] Upon oxidation, the solution color turned to deep purple. The ESR spectrum of the solution of **1** showed a strong unimodal signal ($g = 2.0028$) without any absorption at $g = 2.0078$ ascribed to the oxidizing agent of the thianthrene radical. The half-life of the polyradical **1** was estimated by the ESR signal intensity to be 3.1 weeks at room temperature. The aminium radical integrated in the highly branched phenylenevinylene structure was chemically stable in comparison with that (1.8 weeks) for the linear-type aminium polyradical, poly(4-diphenylaminium-1,2-phenylenevinylene), under the same conditions.

The content of the aminium cation radical or spin concentration (spin per the amine site) was chemically determined by the titration of **1** with *n*-tetrabutylammonium iodide (a chemical quenching or reduction of the radical with the reductant iodide ion.[14c,16]). Aminium radicals are known to be reduced to amines with iodide ion. The spin concentration based on the titration was 0.65 for **1** with DP = 12 (herein after, the reported spin concentration is based on the iodometric titration of the sample).

After the iodometric reduction of the polyradical **1**, the (quenched) polymer sample was sufficiently washed and examined by ^1H NMR spectroscopy. The NMR spectra were in fair agreement with those of the starting amine polymer (see Supporting Information), indicating the appreciable retention of the chemical (especially π-conjugated) structure during the radical generation in **1**.

The diluted solution of the polyradical **1** was transferred to a mica surface and subjected to atomic and magnetic force microscopies (AFM and MFM, respectively). A globular image was detected on the mica, and the single-molecular size corresponded to the molecular weight of the polyradical; a horizontal distance of ca. 15 nm and a vertical distance of ca. 2 nm were estimated for **1** with DP = 12 (Figure 4). The following MFM clearly indicated a magnetic gradient response exactly on the AFM molecular position. The MFM image of the polyradical molecule disappeared after measurement for 1 week, which corresponded to inactivation of the radical in the solid state under ambient conditions.[17]

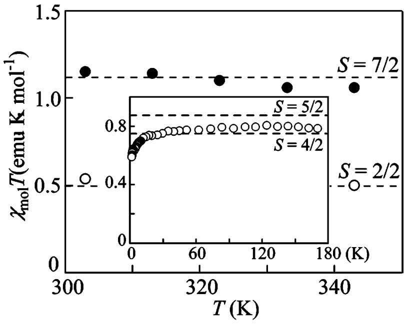

Figure 5. $\chi_{mol}T$ vs T plots for **1** with DP = 12 and spin concentration = 0.65 (●) and Yang's biradical[19] (○). The $\chi_{mol}T$ values were estimated by the NMR shift method. Inset: $\chi_{mol}T$ plots obtained by the SQUID magnetization measurement for the **1** sample with the spin concentration = 0.45.

The magnetic susceptibility (χ) of the aminium cation polyradical **1** in the frozen acidic CH_2Cl_2 solution was measured on a superconducting quantum interference device (SQUID) in the low-temperature range of 1.8−170 K. The inset of Figure 5 shows the $\chi_{mol}T$ vs T plots obtained for the **1** sample (spin concentration = 0.45). The constant $\chi_{mol}T$ value of ca. 0.8 indicated a high-spin state or a strong spin-exchange interaction in the polyradical **1**.

Magnetization of the aminium cation polyradical **1** was also measured by the NMR shift method and Evans equation[18] in acidic CD_2Cl_2 solution: The χ value was estimated by measuring the standard peak shift of cyclohexane for a concentration series of the polyradical solution.[19] The $\chi_{mol}T$ value for the **1** sample with DP = 12 and a spin concentration of 0.65 at room temperature (303 K) corresponded to spin quantum number (S) = $^7/_2$ (Figure 5). The **1** sample with DP = 12 and spin concentration = 0.35 was prepared by oxidation with 0.5 equiv of thianthrene tetrafluoroborate, which gave an $\chi_{mol}T$ value of 0.355 that corresponded to ca. $S = {}^4/_2$ at room temperature. These results suggested that the multiplet state is a stable ground state with a large multiplet−singlet gap or a very strong spin exchange interaction between the unpaired electrons for **1** (however, it does not rule out the possibility of a degenerate singlet−multiplet state). Although the spin (radical) concentration of the **1** sample was not high, the generated radicals' spins did accumulate on the inside of the dendritic amine moiety of the hyperbranched polymer to realize the relatively high S values. The high-spin state of **1** was maintained in the high-temperature range of 303−343 K, as shown in Figure 5. These demonstrated both the chemical stability and the strong spin-exchange interaction of **1**.

The results in this paper concluded that the aminium polyradical **1** behaves as a multiplet molecule ($S = {}^7/_2$ for **1**, with DP = 12 and spin concentration of 0.65) even at room temperature.

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(14) Thianthrene radical is soluble in organic solvents, is a strong oxidizing agent ($E^{\circ\prime}$ = 1.38 V vs Ag/AgCl), and is widely utilized to oxidize triarylamines. (a) Boduszek, B.; Shine, H. J. *J. Org. Chem.* **1988**, *53*, 5142. (b) Murata Y.; Shine, H. J. *J. Org. Chem.* **1969**, *34*, 3368. (c) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877.

(15) It is known that trifluoroacetic acid stabilizes organic cation radicals; for example, Hammerich, O.; Nils, S. M.; Parker, V. D. *J. Chem. Soc., Chem. Commun.* **1972**, 156.

(16) Eberson, L.; Larsson, B. *Acta Chem. Scand.* **1987**, *B41*, 367.

(17) Although the MFM image of the polyradical disappeared after 1 week, the AFM molecular image remained intact even after the complete disappearance of the MFM image. Such a magnetic response could not be detected for the polyradical **1** sample with the lower spin concentration and S by applying the same procedure. The polyradical **1** with $S = {}^7/_2$ and a large magnetization enabled the MFM detection.

(18) (a) Evans, D. F. *J. Chem. Soc.* **1959**, 2003. (b) Cotton, F. A.; Murillo, C. A.; Wang, X. *Inorg. Chem.* **1999**, *38*, 6294.

(19) As the control, the $\chi_{mol}T$ value for a well-known triplet molecule, Yang's biradical,[9] was used under the same measurement conditions.

Experimental Section

The ABB′ type monomer *N*-(3-bromo-4-vinylphenyl)-*N*-(4-methoxyphenyl)-*N*-(4-vinylphenyl)amine **1** was synthesized via six steps, as described below.

4-[*N*-(4-Methoxyphenyl)amino]benzaldehyde. *p*-Bromobenzaldehyde (4.45 g, 24.5 mmol), *p*-anisidine (3.55 g, 28.9 mmol), $Pd_2(dba)_3$ [dba = dibenzylideneacetone; 275 mg, 0.300 mmol], BINAP [2,2′-bis(diphenylphosphino)-1,1′-binaphthalene; 562 mg, 0.902 mmol], Cs_2CO_3 (11.8 g, 36.1 mmol), and toluene (48.1 mL) were placed in a 50 mL ampule. The ampule was degassed and sealed. The mixture was heated to 100 °C for 16 h, poured into dilute aqueous ammonia, and extracted with chloroform. The extract was washed with water, dried, evaporated, and then purified by silica gel column separation with hexane/$CHCl_3$ (5/1) as the eluent. The recrystallization from hexane−$CHCl_3$ gave an orange plate crystal of 4-[*N*-(4-methoxyphenyl)amino]benzaldehyde (3.69 g, yield 67%): mp = 113 °C; IR (KBr pellet) 3585 (ν_{N-H}), 1726 ($\nu_{C=O}$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 9.76 (s, 1H, aldehyde), 7.71−6.84 (m, 8H, aryl), 6.05 (s, 1H, amine), 3.83 (s, 3H, methoxy); ^{13}C NMR ($CDCl_3$) δ = 190.25, 157.03, 151.43, 132.59, 132.20, 127.83, 125.10, 114.84, 133.38, 55.52; mass calcd for M 227.3, found (*m*/*z*) 227 (M^+). Calcd for $C_{14}H_{13}NO_2$; C, 74.0; H, 5.8; N, 6.2. Found: C, 74.6; H, 5.7; N, 6.3.

4-[*N*-(3-Bromo-4-formylphenyl)-*N*-(4-methoxyphenyl)amino]benzaldehyde. 2-(2-Bromo-4-iodo)-1,3-dioxolane[4d] (5.52 g, 17.8 mmol), 4-[*N*-(4-methoxyphenyl)amino]benzaldehyde (3.67 g, 16.2 mmol), $Pd_2(dba)_3$ (185 mg, 0.202 mmol), BINAP (371 mg, 0.606 mmol), Cs_2CO_3 (7.89 g, 24.2 mmol), and toluene (32 mL) were sealed in an ampule and heated to 100 °C for 64 h. The mixture was poured into dilute aqueous ammonia and extracted with chloroform. The extract was washed with water, dried, evaporated, and then purified by silica gel column separation with hexane/$CHCl_3$ (5/1) as the eluent. Recrystallization from methanol gave a yellow powder of 4-[*N*-(3-bromo-4-formylphenyl)-*N*-(4-methoxyphenyl)amino]benzaldehyde (3.48 g, yield 53%): mp = 138.0 °C; IR (KBr pellet) 1576 ($\nu_{C=O}$), 1324 (ν_{C-N}), 1246 (ν_{C-O-C}), 1028 cm^{-1} (ν_{C-O-C}); ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 10.18 (s, 1H, aldehyde), 9.90 (s, 1H, aldehyde), 7.80−6.95 (m, 11H, aryl), 3.85 (s, 3H, methoxy); ^{13}C NMR ($CDCl_3$) δ = 190.40, 190.12, 158.43, 152.59, 151.31, 137.37, 131.70, 131.28, 130.77, 128.84, 128.46, 128.43, 124.92, 122.95, 120.12, 115.63, 55.52; mass calcd for M 410.3, found (*m*/*z*) 410 (M^+). Calcd for $C_{21}H_{16}BrNO_3$: C, 61.5; H, 3.9; N, 3.4. Found: C, 61.4; H, 3.9; N, 3.4.

***N*-(3-Bromo-4-vinylphenyl)-*N*-(4-methoxyphenyl)-*N*-(4-vinylphenyl)amine (3).** Methyltriphenylphosphonium bromide (586 mg, 1.64 mmol) was placed in a Schlenk tube, and *n*-butyllithium (0.513 mL, 0.820 mmol) was injected to form an ylide after the addition of anhydrous THF (0.4 mL). 4-[*N*-(3-Bromo-4-formylphenyl)-*N*-(4-methoxyphenyl)amino]benzaldehyde (67.4 mg, 0.164 mmol) was added and stirred for 30 min. The mixture was extracted with chloroform, and the extract was washed with water, dried, and evaporated. Flash chromatography (silica gel, hexane/$CHCl_3$ 7/1) gave a pale yellow oil of *N*-(3-bromo-4-vinylphenyl)-*N*-(4-methoxyphenyl)-*N*-(4-vinylphenyl)amine (46.1 mg, yield 69%): IR (KBr pellet) 1325 cm (ν_{C-N}), 1242 (ν_{C-O-C}), 1036 cm^{-1} (ν_{C-O-C}); ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.39−6.84 (m, 11H, aryl), 6.98 (dd, *J* = 11 and 17 Hz, 1H, vinyl), 6.65 (dd, *J* = 11 and 18 Hz, 1H, vinyl), 5.64 (d, *J* = 18 Hz, 1H, vinyl), 5.57 (d, *J* = 17 Hz, 1H, vinyl), 5.23 (d, *J* = 11 Hz, 1H, vinyl), 5.16 (d, *J* = 11 Hz, 1H, vinyl), 3.80 (s, 3H, methoxy); ^{13}C NMR ($CDCl_3$) δ = 156.81, 148.44, 146.76, 139.56, 136.10, 135.11, 132.31, 130.27, 127.62, 127.15, 126.73, 125.18, 124.03, 123.44, 120.95, 114.99, 114.40, 112.45, 55.46; mass calcd for M 406.3 found (*m*/*z*) 406 (M^+). Calcd for $C_{23}H_{20}BrNO$: C, 68.0; H, 5.0; N, 3.5. Found: C, 67.7; H, 4.8; N, 3.3

Poly(1,2,(4)-phenylenevinyleneanisylamine) (2). *N*-(3-Bromo-4-vinylphenyl)-*N*-(4-methoxyphenyl)-*N*-(4-vinylphenyl)amine (202 mg, 0.497 mmol), $Pd(OAc)_2$ (2.23 mg, 1.60 μmol), P(*o*-tolyl)$_3$ (12.1 mg, 39.8 μmol), LiCl (210 mg, 4.97 mmol), triethylamine (0.166 mL, 1.19 mmol), and *N*,*N*-dimethylformamide (DMF; 2.49 mL) were heated to 100 °C for 1 h. The THF-soluble part was purified on a polystyrene gel column. Reprecipitation from the chloroform solution into methanol and freeze-drying produced a yellow powder of poly(1,2,(4)-phenylenevinyleneanisylamine) (79 mg yield 39 wt %): IR (KBr pellet) 1242 (ν_{C-O-C}), 1038 (ν_{C-O-C}), 961 cm^{-1} ($\delta_{C=C}$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.36−6.39 (m, 13H, aryl), 5.69−5.48 (m, 0.96H, vinyl), 5.30−5.18 (m, 0.54H, vinyl), 5.18−5.08 (m, 0.42H, vinyl), 3.81 (s, 3H, methoxy); UV/vis (dichloromethane) λ_{max} = 362 nm ($\epsilon = 1.0 \times 10^4$ cm^{-1} M^{-1}, 315 nm ($\epsilon = 9.4 \times 10^3$ cm^{-1} M^{-1}); fluorescent (dichloromethane) λ_{em} = 492 nm (λ_{ex} = 313 nm); GPC (calibrated with polystyrene standard) M_w = 4000, M_w/M_n = 2.0. Calcd for $C_{276}H_{229}BrN_{12}O_{12}$ (DP = 12): C, 83.1; H, 5.8; Br, 2.0; N, 4.2. Found: C, 83.3; H, 5.8; Br, 1.9; N, 4.0.

p-Bromoanisole (0.281 mL, 2.26 mmol) was mixed with poly(1,2,-(4)-phenylenevinyleneanisylamine) (79 mg), $Pd(OAc)_2$ (10.1 mg, 4.52 × 10^{-5} mol), P(*o*-tolyl)$_3$ (55.1 mg, 1.81 × 10^{-4} mol), LiCl (95.6 mg, 2.26 mmol), triethylamine (0.756 mL, 5.42 mmol), and DMF (2.5 mL) and then heated to 100 °C for 3 h. The THF-soluble mixture was purified by a polystyrene gel column. Reprecipitation from the chloroform solution into methanol and freeze-drying produced a yellow powder of the end-capped poly(1,2,(4)-phenylenevinyleneanisylamine) (**2**) (79.7 mg, yield 100 wt %): IR (KBr pellet) 1244 (ν_{C-O-C}), 1036 (ν_{C-O-C}), 960 cm^{-1} ($\delta_{C=C}$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.52−6.15 (m, aryl), 3.78 (s, methoxy); UV/vis (dichloromethane) λ_{max} = 300 nm ($\epsilon = 2.1 \times 10^4$ cm^{-1} M^{-1}), 385 nm ($\epsilon = 2.3 \times 10^4$ cm^{-1} M^{-1}); fluorescent (dichloromethane) λ_{em} = 505 nm (λ_{ex} = 430 nm); GPC M_w = 5200, M_w/M_n = 2.1.

Model Reaction. *N*-(4-Methoxyphenyl)-*N*-(3-methyl-4-vinylphenyl)-*N*-(4-vinylphenyl)amine **4** (10 mg, 29.3 μmol), *p*-bromobenzene (460 mg, 29.3 μmol), $Pd(OAc)_2$ (0.13 mg, 0.579 μmol), P(*o*-tolyl)$_3$ (0.72 mg, 2.37 μmol), LiCl (12.4 mg, 0.93 mmol), triethylamine (7.15 mg, 0.703 μmol), and DMF (0.15 mL) were heated to 100 °C for 48 h. The mixture was extracted with chloroform, and the extract was washed with water, dried, and evaporated to yield the purified reaction mixture.

Preparation of the Polyradical. The thianthrene cation radical tetrafluoroborate (4.00 mg, 13.2 μmol) was dissolved in a mixed solvent (0.92 mL) of CH_2Cl_2/trifluoroacetic acid/trifluoroacetic anhydride = 97/0.6/2.6 (v/v/v). The solution was dropped into the trifluoroacetic acid (40.9 μL) solution of **2** (1 mg, 2.36 μmol), and stirred for 5 min at room temperature (the resultant solution composition was CH_2Cl_2/trifluoroacetic acid/trifluoroacetic anhydride = 81/17/2 v/v/v).

Cyclic and Differential Pulse Voltammetry. Cyclic voltammetry and differential pulse voltammetry were recorded for the 1 mM **2** in the 0.1 M tetrabutylammonium tetrafluoroborate−CH_2Cl_2 solution by use of a BAS 100B/W electrochemical analyzer (Bioanalytical Systems, Inc.). The working electrode, the counterelectrode, and the reference electrode were a platinum disk, a platinum wire, and a saturated Ag/AgCl calibrated versus a ferrocene couple, respectively.

Stopped-Flow and Electrolytic ESR and UV/Vis Spectroscopies. Anhydrous CH_2Cl_2 solutions of 0.1 mM **2** and 2 mM $NOSbF_6$ solubilized with 18-crown-6 were mixed in the spectrophotometer. The time-resolved UV/vis spectrum was recorded on a rapid-scan stopped-flow spectrophotometer RSP-501 (Unisoku Co., Osaka, Japan). Compound **2**, 0.1 mM in the CH_2Cl_2 solution containing 0.1 M $(C_4H_9)_4NBF_4$, was oxidized with a platinum gauze (100 mesh) electrode at a given potential by use of a potentiogalvanostat NPGS-301 (Nikko Keisoku Co., Kanagawa). The ESR and UV/ vis spectra were recorded on a JEOL JES-2XG ESR spectrometer and a Jasco V-550 UV/vis spectrophotometer. The ESR signal was calibrated with an external standard of Mn^{2+}/MgO (*g* = 1.981).

AFM and MFM Measurements. A drop of 1−5 μM dichloromethane solution of the polyradical **1** was transferred onto freshly cleaved mica with a microsyringe, and then the solvent was carefully removed by air-drying. If a concentrated solution was used, the polymer was aggregated on the surface. The AFM and MFM experiments were performed on a Nanoscope III (Digital Instruments, Inc.). A single-crystal silicon cantilever for AFM (Digital Instruments; NCH; tip height 10−15 μm, radius curvature at front ca. 5 nm, length 125 μm, width 30 μm, and thickness 3−5 μm, with a spring constant between 20 and 100 Nm^{-1}) was used. Resonance peaks in the frequency response of the cantilever were selected in the range between 280 and 320 kHz for the tapping-mode oscillation. A commercially available and standard MFM tip coated with a ferromagnetic CoCr alloy with a length of 225 μm and a magnetic moment of 10^{-13} emu (purchased from Digital Instruments, Nanoprobe SPM Tips type MESP) was used. All tips were magnetized in the *z*-direction, which is along the long tip axis. The MFM images in the noncontact mode were obtained after the AFM imaging in the tapping mode in the same scan area with a scan rate of 2 Hz, a drive resonance frequency of ca. 78 kHz, and a scan lift height of 20 nm, which were selected upon tuning.

Magnetic Susceptibility Measurement with NMR. Thin NMR tubes filled with 2 vol % cyclohexane-mixed sample solution were placed in the center of a thick standard NMR tube (a 5 mm i.d. glass tube) which was filled with the mixture of the deutrated solvent C_6D_6 and cyclohexane for the external reference, and the NMR spectrum was recorded at 499.10 MHz on a JEOL NMR 500 Λ spectrometer. The chemical shift of cyclohexane was measured, and the magnetic susceptibility was calculated on the basis of the Evans equation[18] from $\Delta\nu$, which is the frequency separation of cyclohexane between those of the internal sample solution and the external reference for the radical solutions at concentrations of 9.5, 6.3, 3.2, and 0 mM. The accuracy of these methods was confirmed by measurement of $Cr(acac)_3$, in which the solution composition and concentration were equivalent to the other measurements [the external reference was C_6D_6 containing 2 vol % cyclohexane; the internal reference was the mixed solution CH_2Cl_2/trifluoroacetic acid/trifluoroacetic anhydride (81/17/2 v/v/v) containing 2 vol % cyclohexane].

SQUID Measurement. The magnetization and static magnetic susceptibility were measured on a Quantum Design MPMS-7 SQUID magnetometer. The static magnetic susceptibility was measured from 1.8 to 200 K in a 0.5 T field. The magnetization was measured from 0.5 to 7 T at 1.8, 2, 2.5, and 5 K. Ferromagnetic impurities and diamagnetic susceptibility of the matrix and the capsule were determined by Honda-Owen and Curie plots, respectively, and were subtracted from the measured magnetization.

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Supporting Information Available: Data of the model reaction, chemical reduction of **1**, ESR spectrum of **1,** data of the NMR shift measurement, and other measurements. This material is available free of charge at http://pubs.acs.org.

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