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A High-Spin and Durable Polyradical: Poly(4-diphenylaminium-1,2-phenylenevinylene)

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A purely organic, high-spin, and durable polyradical molecule was synthesized: It is based on the non-Kekulé- and non-disjoint design of a π-conjugated poly(1,2-phenylenevinylene) backbone pendantly 4-substituted with multiple robust arylaminium radicals. 4-*N*,*N*-Bis(4-methoxy- and -*tert*-butylphenyl)amino-2-bromostyrene **5** were synthesized and polymerized with a palladium−phosphine catalyst to afford the head-to-tail-linked polyradical precursors (**1**). Oxidation of **1** with the nitrosonium ion solubilized with a crown ether gave the aminium polyradicals ($\mathbf{1}^+$) which were durable (half-life > 1 month) at room temperature in air. A high-spin ground state with an average $S = (4.5)/2$ for $\mathbf{1a}^+$ was proved even at room temperature by magnetic susceptibility, magnetization, ESR, and NMR measurements.

Introduction

Much effort has been expended during the past decade on synthesizing high-spin and purely organic molecules which are predicted to be a molecular magnetic material with an unknown magnetism.[1] Synthesis of π-conjugated organic polyradical molecules designed along a non-Kekulé and nondisjoint[2] fashion for the connectivity of the multiradicals is one of the most effective approaches because the ferromagnetic spin alignment between unpaired electrons through the π-conjugation can be made strong.[3] The recent progress in this field is based on the synthesis of the highly cross-linked, ladderlike, dendritic, and hyper-branched polyradicals.[4,5] The huge magnetic moment and the magnetic spin ordering of *S* (spin quantum number) >5400 were eventually attained at low temperature for the highly cross-linked network of macrocyclic triarylmethine units.[6] However, the triarylmethine radical can survive only below 200 K, so chemically stable radical species are desired in such a cross-linked polyradical in order to raise the magnetic ordering temperature and to provide feasibility as a material.[3e]

In parallel to the cross-linked polyradicals, there still remains another synthetic procedure, which focuses on a π-conjugated linear polymer bearing multiple pendant radical groups as a classical, one-dimensional model molecule. The pendant radical groups are attached to one π-conjugated backbone that satisfies the non-Kekulé structure and nondisjoint connectivity among the nonbonding molecular orbitals of the radicals' unpaired electrons. Such linear polyradicals bearing pendant spin sources possess the following advantages.[3c,d] First, a ferromagnetic spin interaction occurs through the π-conjugated backbone and potentially even works over a long range. That is, the spin coupling is not sensitive to the defects that are unavoidable for macromolecular polyradicals. Second, a great number of spins are accumulated along one backbone or within one molecule. The spins are expected to interact not only with their neighboring spins but also with more remote spins. Third, precursors of these types of polyradicals can be synthesized via a one-pot polymerization, and they and the polyradicals themselves are soluble in common solvents; these are very favorable for obtaining well-defined samples to study. Fourth, various chemically stable radical species can be introduced into a polyradical as the pendant group. The resultant polyradical has substantial stability and is easily handled, e.g., at room temperature in air. Such feasibility would be indispensable for the future application of magnetic organic molecules as materials.

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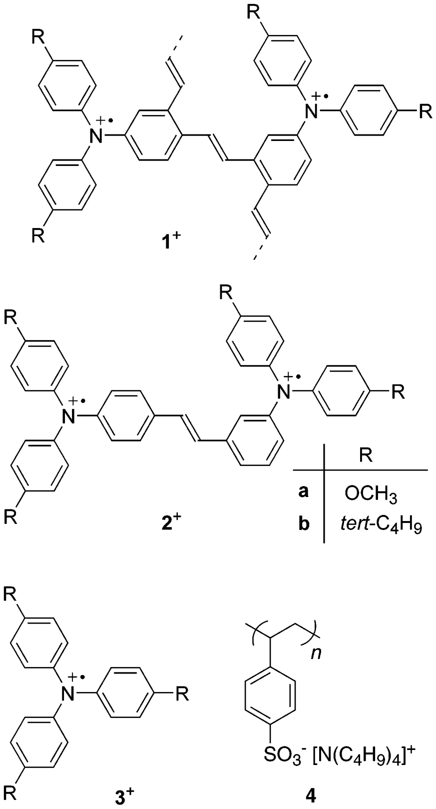
Along with this molecular designing, we have succeeded in realizing an intramacromolecular high-spin alignment among the pendant unpaired electrons by synthesizing poly(1,2-phenylenevinylene)s that are 4-substituted with the 3,5-di-*tert*-butyl-4-oxyphenyl,[7] *N*-*tert*-butyloxyamino,[8] galvinoxyl, or nitronylnitroxide groups.[9] The poly(1,2-phenylenevinylene) backbone was characterized as being relatively coplanar with an extended π-conjugation even after the introduction of the pendant radical groups.

Besides the backbone structure, a spin source, which is to be pendantly introduced into the π-conjugated backbone, should be carefully selected from the list of radical species in order to provide both a sufficient ferromagnetic spin exchange interaction and chemical stability for such linear polyradicals. It is known that triaryl aminium cationic radicals derived from the para-substituted triphenylamines are quite stable and are often used as an oxidizing reagent and a catalyst in redox reactions.[10] In addition, the spin density of the aminium radicals delocalizes into the three attached aryl groups, which would efficiently work in the spin-exchange interactions. The aminium cationic radical is a favorable candidate for the spin source to be utilized in a chemically durable and high-spin polyradical. From such viewpoints, a series of oligomeric, cyclic, and polymeric aminium radicals were derived from *m*-phenylene-connected and cross-linked polyarylamines. Their magnetic behaviors have already been reported.[11] However, the aminium cationic radicals were formed in a cross-conjugation style within the backbone for these molecules, which did not belong to the type of linear polymer bearing pendant radicals and often lacked solvent solubility that leads to a limitation of the radical (spin) generation yield. On the other hand, we have synthesized the aminium cationic diradical of 3,4′-bis[*N*,*N*-bis(4-methoxy- and -*tert*-butylphenyl)amino]stilbene, **2a**$^{+}$ and **2b**$^{+}$, as a durable triplet molecule.[12] We have recently extended the diradical **2b**$^{+}$ to a high-spin polyradical **1b**$^{+}$ and preliminarily reported a half-life of 1.5 days and a high-spin multiplicity of $S = 3/2$ for **1b**$^{+}$ even with the spin concentration of ca. 0.4 spin per unit at room temperature.[13] In this study, we synthesized the pendant-type poly(aminium cationic radical)s based on poly(1,2-phenylenevinylene), **1a**$^{+}$ and **1b**$^{+}$, with well-defined chemical structures, and described the magnetic properties of the durable polyradicals with $S = (4.5)/2$ even at room temperature.

CHART 1



Results and Discussion

Monomer Synthesis and Polymerization A head-to-tail linkage structure of the radical group-bearing monomer unit is essential for the non-Kekulé and non-disjoint requisite or the following magnetic study; this was established through the polycondensation via the Heck reaction of the 4-radical precursor-substituted 2-bromostyrene in this paper. 4-(*N*,*N*-bis(4-methoxyphenyl)amino)-2-bromostyrene **5a** and 4-(*N*,*N*-bis(4-*tert*-butylphenyl)amino)-2-bromostyrene **5b** were synthesized as the monomers for the polycondensation. Each para position of the triphenylamine is protected with the methoxy, *tert*-butyl, or the vinylene group in order to suppress dimerization and/or disproportionation of the formed aminium cationic radical (see the structure of **1**$^{+}$). *N*,*N*-Bis(4-methoxyphenyl)amine and *N*,*N*-bis(4-*tert*-butylphenyl)amine were prepared by cross-coupling reaction between the 4-subsituted aniline and the 4-substituted bromobenzene. 2-Bromo-4-iodotoluene was brominated with *N*-bromosuccinimde (NBS) and converted to 2-bromo-4-iodobenzaldehyde via the Sommelet rearrangement (Scheme 1).[14] After its formyl group was protected with the 1,3-dioxolane group, the palladium-catalyzed amination of **6** with bis(4-methoxyphenyl)amine followed by deprotection yielded **7**. The formyl group of **7** was converted to a vinyl group via the Wittig reaction to afford the bromostyrene derivative **5a** as the styrene monomer. On the other hand, to obtain **5b**, *N*,*N*-bis(4-

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(7) (a) Nishide, H.; Kaneko, T.; Nii, T.; Katoh, K.; Tsuchida, E.; Yamaguchi, K. *J. Am. Chem. Soc.* **1995**, *117*, 548. (b) Nishide, H.; Kaneko, T.; Nii, T.; Katoh, K.; Tsuchida, E.; Lahti, P. M. *J. Am. Chem. Soc.* **1996**, *118*, 9695.

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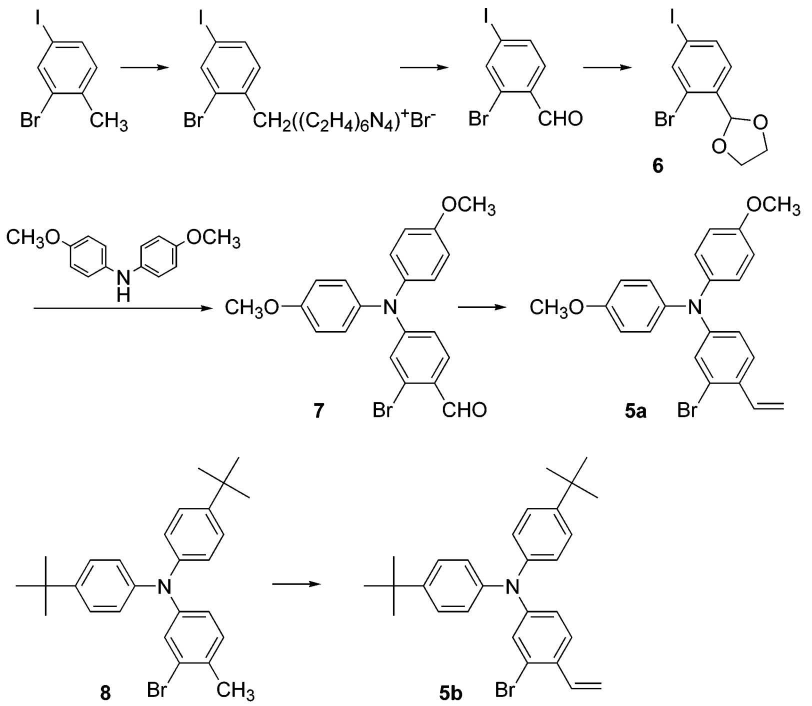
SCHEME 1



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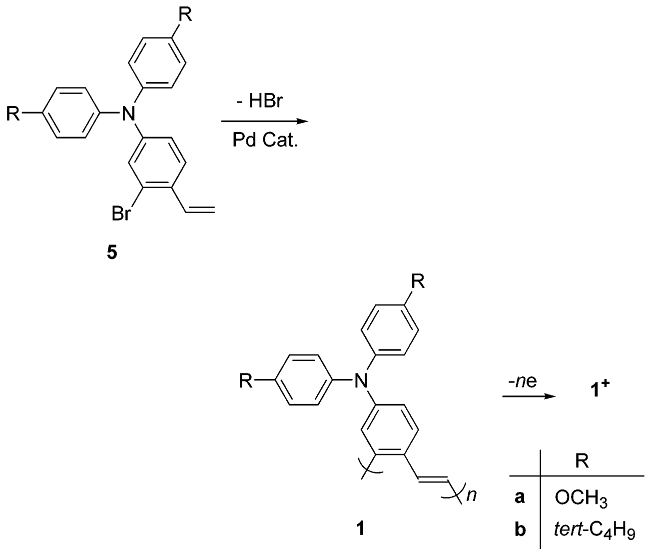

tert-butylphenyl)amine was introduced onto the 2-bromo-4-iodotolulene by selective coupling at the iodo position using the palladium catalyst with BINAP as a hindered and bidentate ligand, to efficiently afford 2-bromo-4-(*N*,*N*-bis(4-*tert*-butylphenyl)amino)toluene **8**. The methyl group of **8** was brominated with NBS and converted to a vinyl group via the Wittig reaction to yield the styrene monomer **5b**.

The bromostyrene derivatives, **5a** and **5b**, were polycondensed (Scheme 2) through the Heck reaction using the catalyst of palladium acetate and tri(*o*-tolyl)phosphine in the presence of triethylamine and lithium chloride as a base and a source of chloride ion,[15,16] respectively, in DMF solution at 70 °C for 72 h (see Table 3 in the Experimental Section). These polymerization conditions were selected for the selective β-arylation of the vinyl group with the aryl bromide of **5**, based on the following ^{13}C-labeled control reaction using 2-bromo-5-hexyloxy(*2*-^{13}*C*)styrene **9** as the monomer. The Heck cross-coupling reaction of monosubstituted olefins and aryl halides has been characterized by the formation of a β-arylated product with the high stereoselectivity of the *trans*-vinylene structure but still involves an α-arylation byproduct (Scheme 3).[17] In this study, the α-arylation means a defect formation in the formed poly(1,2-phenylenevinylene). The ^{13}C-labeled bromostyrene was polymerized with the palladium-tri(*o*-tolyl)phosphine catalyst in the presence of 5.0−15 vol % triethylamine, 0.0−5.0 M lithium chloride, at 70−100 °C, in DMF. For example, the poly(1,2-phenylenevinylene) at 100 °C and without the lithium chloride addition gave the ^{13}C NMR spectrum, which involved the slight signal at 120.0 ppm assigned to the α-arylation structure of $RR'C{=}^{13}CH_2$ (see the Supporting Information). The ^{13}C NMR spectrum of the polymer, obtained under the reaction conditions stated at the top of this paragraph, indicated a completely poly(1,2-phenylenevinylene) structure without any α-arylation defect. In the ^{1}H NMR spectra of **1** obtained under these selected conditions, there were also no signals assigned to the 1,1-diphenylethylene linkage (ca. 6.9 ppm) as the defect and the 1,2-*cis*-stilbene moiety (ca. 6.5 ppm) as a conformer, supporting the head-to-tail linked primary structure of **1**, at least, based on the ^{13}C NMR analysis.

The polymers **1** were soluble in common solvents such as methylene chloride, chloroform, tetrahydrofuran, ben-

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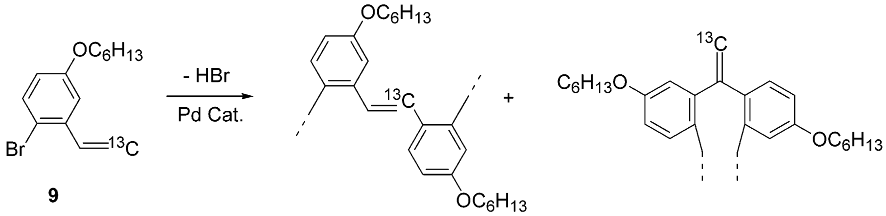
SCHEME 3



zene, toluene, triethylamine, and DMF. The degree of polymerization (DP) of **1** was measured by GPC using polystyrene standards, and the terminal bromine contents were 12.5 and 12.8, respectively, for **1a**, and 13.0 and 12.4, respectively, for **1b**. The polydispersity (the ratio of number- and weight-average molecular weight) was 1.3 and 1.4 for **1a** and **1b**, respectively. These also supported the primary structure of **1**.

The chloroform solution of the greenish yellow polymers, **1a** and **1b,** showed two UV/vis absorption maxima at 301 and 369 and 306 nm and 365 nm, respectively, with the molar absorption coefficient $\epsilon = 2 \times 10^4$ and 1×10^4 M^{-1} cm^{-1}, respectively. They are ascribed to the triarylamine moiety (λ_{max} = ca. 300 nm) and the *trans*-stilbene moiety. The visible absorption was extended to 525 and 510 nm for **1a** and **1b**, respectively, in comparison with that of poly(1,2-phenylenevinylene) (ca. 430 nm).

The solutions of **1**−**3** exhibited strong photoluminescences. The λ_{em} for **1a** and **1b** were 530 and 512 nm, respectively, in the chloroform solution (λ_{ex} = 312 nm) and were bathochromically shifted in comparison with those for **2a** and **2b** (491 and 460 nm, respectively) and for **3a** and **3b** (398 and 360 nm, respectively). The bathochromic shift of λ_{em} for **1** corresponds to the longer wavelength shift of the UV absorption edges of **1**, suggesting a developed π-conjugation for **1**.

Oxidations to the Aminium Radicals Cyclic voltammetry of **1**−**3** in the methylene chloride solution with tetrabutylammonium tetrafluoroborate as the electrolyte gave unimodal waves which were repeatedly recorded in the potential sweeps of, e.g., 100 times at room temperature (example, see the inset of Figure 1). The voltammogram result means that the triarylamine groups are electrochemically oxidized to the aminium cationic radicals and reduced to the amines without any subsequent chemical side reactions, such as the dimerization to form a benzidine and a disproportionation. This also suggested that the electrostatic repulsion was not strong among the adjacent aminium cationic groups along the π-conjugated chain to produce a separation in the redox waves (differential pulse voltammetry of **1** and **2** also gave simple unimodal oxidation waves).

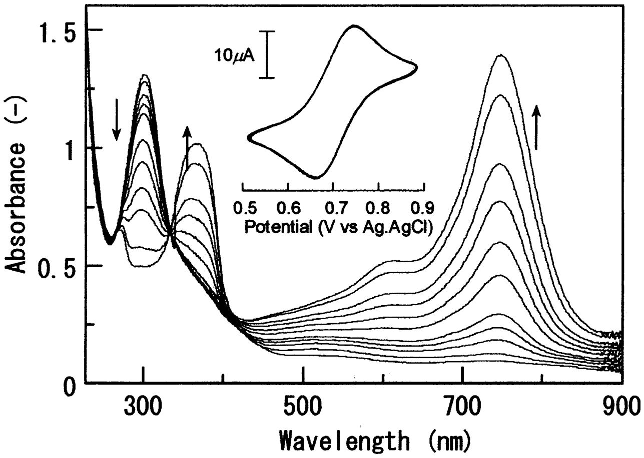


FIGURE 1. UV/vis absorption spectral change of **1a** solution under the electrolytic potential given from 0.50 to 0.85 V at room temperature. 0.05 mM (amine unit) methylene chloride solution of **1a** with 0.1 M $(C_4H_9)_4NBF_4$ as the supporting electrolyte. Inset: cyclic voltammogram of **1a** in the same methylene chloride solution with sweep rate of 100 mV/s.

TABLE 1. Redox Potential ($E_p^{1/2}$) and Peak Separation (ΔE_p^{a-c}) of the Polymer 1, the Dimer 2, and the Monomer 3[a]

	methoxy-substituted **a**		*tert*-butyl-substituted **b**	
amine	$E_p^{1/2}$ (V)	ΔE_p^{a-c} (V)	$E_p^{1/2}$ (V)	ΔE_p^{a-c} (V)
1	0.81	0.18	0.92	0.22
2	0.78	0.18	0.94	0.17
3	0.68	0.17	0.89	0.15

[a] Methylene chloride solution of 0.1 M $(C_4H_9)_4NBF_4$, vs Ag/AgCl (ref ferrocene Fc/Fc^+ = 0.58 V), sweep rate: 100 mV/s.

The redox potentials and the potential separation between the anodic oxidation and cathodic reduction peaks are given in Table 1. The redox potentials for the methoxy-substituted **1a**, **2a**, and **3a**, were lower than those for the *tert*-butyl-substituted **1b**, **2b**, and **3b**. This result is clearly explained by the more electron-donating effect of the methoxyl group at the para positions. It is also depicted in Table 1 that the redox potential between the amine and the aminium cationic radical increased in the order of the monomer **3** < the dimer **2** ≤ the polymer **1**. The potential separations between the oxidation and reduction peaks were larger than the theoretical value (58 mV) for an electrochemically reversible reaction and increased as the sweep rate increased during the cyclic voltammetry. The cathodic shift of the redox potential and the broadening or constancy of the redox wave for the dimer, and especially the polymer, could be explained by the delocalization effect of the formed aminium cationic radical in the π-conjugation of the dimer and polymer.

The electrochemical oxidations of the polymer **1a** were monitored by UV/vis absorption spectroscopy, using the assembly of an optically transparent thin-layer platinum minigrid electrode. With the oxidation potential given, there was a decrease in the absorption intensity at 301 nm of the neutral amine and the accompanying appearance of two new absorption bands at 367 and 748 nm with isosbestic points at 267 and 333 nm; the latter values were ascribed to the aminium radicals of triarylamine.[10] The spectral change with isosbestic points supported the quantitative oxidation from **1** to 1^+. The color of the solution turned deep blue upon oxidation.

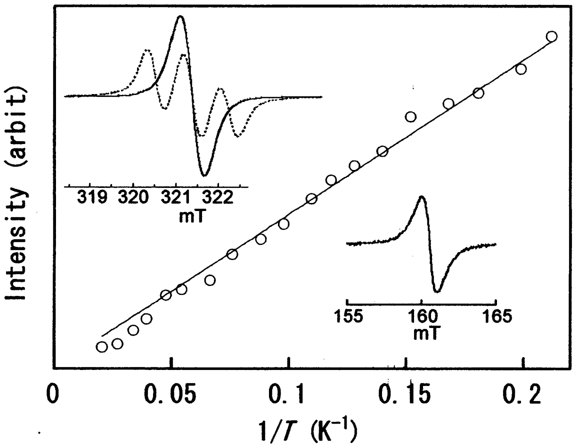


FIGURE 2. Temperature dependency of the ESR signal intensity of the $\Delta M_s = \pm 2$ transition of **1a**$^+$ with 0.90 spins/unit in methylene chloride. The solid line is a least-squares fitting to Curie's law (intensity $= C/T$). Inset: ESR spectra of the **1a**$^+$ methylene chloride solution with a low spin concentration of 0.10 spin/unit (dashed line) and a high spin concentration of 0.89 (solid line) at room temperature, and the $\Delta M_s \pm 2$ spectrum of **1a**$^+$ with spin concentration of 0.80 in methylene chloride at 4.0 K.

Triarylaminium radical salts had been prepared from the corresponding triarylamines using a silver(I) salt in the presence of iodine, a nitrosonium ion salt, and a higher valent halide as the oxidant.[10] We chose, by considering both the oxidation potential of the **1** amines and the counteranion species, the nitrosonium ion salt, e.g., $NOBF_4$ or $NOPF_6$, of which the oxidizing potential has been reported to be 1.58 V.[18] We found that the concentrated methylene chloride solution of $NOBF_4$ or $NOPF_6$ solubilized with the equivalent amount of 18-crown-6-ether was effective for the oxidation and was added dropwise to the dilute methylene chloride solution of the amines **1**−**3** to accomplish a high yield for the aminium cationic radical formation. The spin concentrations for **1a**$^+$ and **1b**$^+$ were estimated to be 0.89 and 0.56 spin/monomer amine unit, respectively, on the basis of the ESR signal intensity. Colors of the methylene chloride solutions of these amines turned from pale yellow to deep blue, which agreed with the UV/vis absorption change during the electrolytic oxidation given in Figure 1.

The stability of the aminium cation radicals **1**$^+$, **2**$^+$, and **3**$^+$ in the solid state depended on the counteranion species. For example, the aminium cation radical salt of **1a**$^+$ with an anion of larger size such as hexafluorophosphate (PF_6^-) did not show any deterioration even after one week at room temperature in air (the half-life estimated by the ESR signal intensity > one month). This half-life was much longer than that for the aminium cation radical salt of **1a**$^+$ with BF_4^- (half-life ca. 2 weeks) and then those previously reported for both the *m*-phenylene-coupled oligo(triphenylamine)s[11] and the poly(1,2-phenylenevinylene)s 4-substituted with 3,5-di-*tert*-butyl-4-oxyphenyl and *N*-*tert*-butyloxyamino.[7,8]

The solution ESR of **1**$^+$ with a low spin concentration gave a three-line spectrum ($a_N = 0.85$ and 0.90 mT for **1a**$^+$ and **1b**$^+$, respectively) with $g = 2.0029$ and 2.0028 for **1a**$^+$ and **1b**$^+$, respectively (inset of Figure 2). These ESR spectra indicate a nitrogen-centered radical formation.[19] With an increasing spin concentration, the ESR spectrum changed to a unimodal spectrum with a peak-to-peak width of 0.69 and 0.81 mT for **1a**$^+$ and **1b**$^+$, respectively.

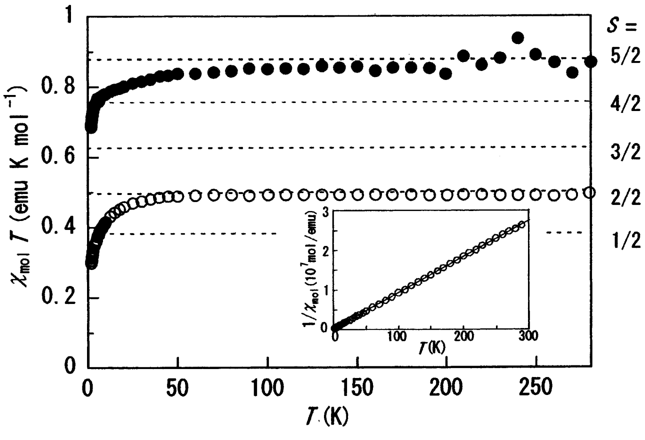


FIGURE 3. $\chi_{mol}T$ vs T plots for the powder sample of **1**$^+$: (○) neat powder of **1a**$^+$ with spin concentration of 0.25; (●) poly(styrenesulfonate tetrabutylammonium) **4**-diluted sample of **1a**$^+$ with a spin concentration of 0.63. Inset: $1/\chi_{mol}$ vs T plots of neat powder of **1a**$^+$.

The ESR study at cryogenic temperatures gave a $\Delta M_s = \pm 2$ (half-field and forbidden) transition at 158 mT for **1**$^+$ (for **1a**$^+$, see the inset of Figure 2). The signal intensity of the $\Delta M_s = \pm 2$ transition for **1a**$^+$ was proportional to the reciprocal of temperature in the range between 4.5 and 100 K and followed Curie's law (Figure 2). This result means that a triplet state ascribed to the $\Delta M_s = \pm 2$ peak is a stable ground state with a large triplet−singlet gap for **1a**$^+$ (however, it does not rule out the possibility of a degenerate singlet−triplet state).

Magnetic Properties The PF_6^- salt of **1**$^+$ was isolated as a blue powder by pouring the methylene chloride solution of **1**$^+$ oxidized with a small excess of $NOPF_6$/18-crown-6-ether into dimethyl ether[20] for the magnetic measurement in the temperature range up to room temperature. Besides the neat sample, **1**$^+$ was also isolated in the presence of polystyrene or ploy(styrenesulfonate tetrabutylammonium) **4** as a diamagnetic diluent. Compound **4** is a polyanion but soluble in methylene chloride: After the solution of **4** was added to the methylene chloride solution of the polyradical **1**$^+$, the mixture became suspended, suggesting the polycation/polyanion complex formation of **1**$^+$ and **4**. These isolated samples were subjected to static magnetic susceptibility (χ) and magnetization (M) measurements using a SQUID magnetometer. χ was normalized to the χ_{mol} values with the radical concentration in the sample determined by the saturation magnetization (M_s) of the M vs magnetic field (H) plots.

Figure 3 shows the $\chi_{mol}T$ vs T plots of **1a**$^+$. The plots are flat in the higher temperature range, although they

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[18] Kochi, J. K. *Acc. Chem. Res.* **1992**, *25*, 39.

[19] The ESR super hyperfine structure was clearly observed for the solution of the monomeric aminium cation radical **3**$^+$; $a_N = 0.846$, $a_{o\text{-H}} = 0.183$, $a_{m\text{-H}} = 0.061$, and $a_{H(methoxy)} = 0.061$ mT for **3a**$^+$ (see the Supporting Information). These spectra supported the delocalization of spin the density in **3**$^+$ onto the attached three aryl groups.

[20] Upon oxidation, NO gas evolved. The precipitated powder was composed of the PF_6^- salt of **1**$^+$ on the basis of the elemental analysis.

TABLE 2. Weiss Temperature (θ) and Spin Quantum Number (S) of the Aminium Polyradicals

aminium radical	degree of polymerization	diluent	spin concn[a] (spin/unit)	θ (K)	S[b]	S[c]
1a$^+$	12.8	none	0.25	-1.7 ± 0.1	(2.0)/2	(1.8)/2
1a$^+$	12.8	polystyrene	0.37	-1.9 ± 0.1	(2.3)/2	(2.2)/2
1a$^+$	12.8	4	0.45	-0.42 ± 0.02	(2.9)/2	(3.2)/2
1a$^+$	12.8	4	0.63	-0.33 ± 0.03	(4.5)/2	(4.7)/2
1a$^+$	7.3	4	0.66	-0.21 ± 0.01	(3.8)/2	(3.5)/2
1b$^+$	12.0	4	0.50	-0.68 ± 0.1	(3.0)/2	(2.8)/2

[a] Determined by the M_s value. [b] Estimated by the magnetization curve as Figure 4. [c] Estimated by the $\chi_{mol}T$ value as Figure 3.

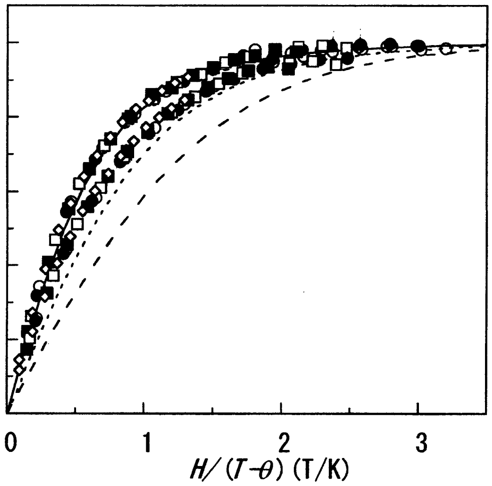

FIGURE 4. Normalized plots of magnetization (M/M_s) vs the ratio of magnetic field and temperature ($H/(T - \theta)$) for the **4**-diluted **1a**$^+$ (DP = 12.8) with spin concentration = 0.63 spin/unit and for the **4**-diluted **1a**$^+$ (DP = 12.8) with spin concentration = 0.45 spin/unit at 1.8 (○), 2 (●), 2.5 (□), 3 (■), and 5 (◇). Theoretical Brillouin curves for $S = 1/2$ (dashed line), 2/2 (broken line), and 4/2 (solid line).

decrease below 50 K. The latter is attributed to an antiferromagnetic (probably through-space) interaction among the **1a**$^+$ molecules, which was significantly suppressed for **1a**$^+$ diluted with **4**. The $1/\chi_{mol}$ vs T plots (inset of Figure 3) obeyed the Curie−Weiss law,[21] indicating the paramagnetic behavior of **1a**$^+$ and giving the Weiss temperature (θ, Table 2). The θ value represents an antiferromagnetic interaction between the unpaired electrons, which was reduced for **1a**$^+$ by the polyion complex formation with **4**.

The normalized plots of magnetization (M/M_{sat}) for **1a**$^+$ diluted with **4** (Figure 4) are close to the Brillouin curves for 4/2 and 5/2, indicating a high-spin ground state for **1a**$^+$. The average S values for the samples of **1a**$^+$ and **1b**$^+$ estimated from the magnetization data are listed in Table 2. The S values were also estimated by applying the Curie−Weiss law[21] to the $\chi_{mol}T$ data (examples in Figure 3) and are also given in Table 2. One notices both that a relatively high spin concentration was realized for the **1a**$^+$ samples diluted, especially with **4**, and that a relatively high S value was observed for those samples with high spin concentrations. For the **1a**$^+$ sample with the lower molecular weight (DP = 7.3) resulted in the small S values. These results concluded that a ferromagnetic and intramolecular spin-alignment is realized between the unpaired electrons of the polyaminium cationic radicals, by taking into account both the molecular weight or DP and the spin concentration of **1a**$^+$.

The $\chi_{mol}T$ plots leveled off in the temperature range from 50 to 280 K in Figure 3 (the fluctuation for **1a**$^+$ diluted with **4** above 230 K is probably ascribed to both the glassy-rubbery transition temperature of the formed polyion complex at 250 K and the lower spin concentration of the diluted sample). The flat $\chi_{mol}T$ plots means that the multiplet ground state for **1a**$^+$ is significantly large ($\sim k_BT$) and that **1a**$^+$ is a paramagnetic molecule with $S = (4.5)/2$. Ferromagnetic coupling effect of the 3,4′-stilbene linker has been reported by using the stilbene diradicals in the previous papers,[7,22] where the triplet−singlet gap (ΔE_{T-S}) for the bis(2′,6′-di-*tert*-butyl-4′-oxyphenyl)- and bis(*N*-*tert*-butyl nitroxide)-substituted stilbene was experimentally estimated to be 72 and 59 K, respectively. The ΔE_{T-S} value was also computationally estimated to be >1000 K for the bis(methyleneradical)-substituted stilbene.[22] Taking into account the spin density delocalization in the triarylaminium cation radical (see the Supporting Information), the very strong spin-exchange interaction observed for **1**$^+$ in this paper is not in conflict with the results in the previous papers.

The magnetic susceptibility of **1**$^+$ was measured at room temperature by the NMR shift method. The $CDCl_3$ solutions of **1a**$^+$ and **1b**$^+$ were prepared by the oxidation of **1** with $NOPF_6$/18-crown-6-ether. The χ_{mol} values were calculated based on the Evans equation,[23] measuring the resonance frequency separation of the cyclohexane standard peak for a concentration series of the **1**$^+$ solution. The calculated $\chi_{mol}T$ values for **1a**$^+$ and **1b**$^+$ in the solution were 0.86 and 0.60 emu·K·mol^{-1} at 300 K, respectively; they corresponded to $S = (4.9)/2$ and (2.8)/2 and were comparable with those of the SQUID measurement in Table 2. These results support the idea of the linear polyradical pendantly substituted with aminium cation in the non-Kekulé and nondisjoint fashion to provide the observed high S value for a purely organic polyradical at room temperature.

Experimental Section

4-[*N*,*N*-Bis(4-methoxyphenyl)amino]-2-bromobenzaldehyde (7). The mixture of 2-bromo-4-iodobenzaldehyde (6.09 g, 19.6 mmol), 1,2-ethanediol (12.2 g, 196 mmol), benzene (9.7 mL), and *p*-toluenesulfonic acid monohydrate (18.6 mg, 0.099 mmol) was refluxed until close to the theoretical amount of water was collected in the trap (ca. 6 h).[24] The reaction mixture

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(21) $\chi_{mol}T = N_A g^2 \mu_B{}^2 TS(S + 1)/3k_B(T - \theta)$, where, N_A, g, μ_B, and k_B are Avogadro's number, g-factor, Bohr magneton, and Boltzman constant, respectively.

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was then extracted with chloroform. The organic layer was dried over anhydrous sodium sulfate and evaporated. The crude product was purified using a silica gel column with a hexane eluent to give 2-(2-bromo-4-iodo-phenyl)-1,3-dioxolane **6** as a white solid (6.96 g): yield 98%; mp 56 °C; ^{1}H NMR (500 MHz, $CDCl_3$; ppm) 7.92 (d, $J = 1.8$ Hz, 1H), 7.66 (dd, $J = 8.1, 1.4$ Hz, 1H), 7.31 (d, $J = 8.1$ Hz, 1H), 6.02 (s, 1H), 4.09 (dd, $J = 3.5, 15.7$ Hz, 4H); ^{13}C NMR (500 MHz, $CDCl_3$; ppm) δ 140.9, 136.6, 136.3, 129.2, 123.6, 102.2, 95.2, 65.5; IR (KBr pellet, cm^{-1}) 3080 (ν_{C-H}), 2952 (ν_{C-H}), 2886 (ν_{C-H}), 943 (ν_{C-O-C}) cm^{-1}; MS (EI) *m/e* 354 ($(M - 1)^+$), 356 ($(M + 1)^+$), calcd for $C_9H_8BrIO_2$ 355.0.

Compound **6** (100 mg, 0.28 mmol) and bis(4-methoxyphenyl)amine (59 mg, 0.26 mmol) were dissolved in toluene (2.1 mL). Sodium *tert*-butoxide (37 mg, 0.38 mmol), tris(dibenzylideneacetone)dipalladium (2.9 mg, 3.2 μmol), and (*S*)-(−)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (6.0 mg, 9.6 μmol) were added, and then mixture was heated at 100 °C for 40 h to yield a reddish brown precipitate. The reaction mixture was neutralized with 1 N aqueous ammonia and extracted with chloroform. The organic layer was washed with brine and evaporated to give the crude product, which was purified using a silica gel column with hexane/ethyl acetate (3/1) to afford 82.7 mg of (3-bromo-4-(1,3-dioxolan-2-yl)phenyl)bis(4-methoxyphenyl)amine as a yellow solid: yield 71%; mp 115 °C; ^{1}H NMR (500 MHz, $CDCl_3$; ppm) δ 7.33 (d, $J = 8.6$ Hz, 1H), 7.05−6.81 (m, 10H), 6.01 (s, 1H), 4.16−4.01 (m, 4H), 3.79 (s, 6H); ^{13}C NMR (500 MHz, $CDCl_3$; ppm) δ 156.5, 150.6, 139.9, 128.1, 127.1, 127.1, 123.3, 122.9, 118.3, 114.9, 102.8, 65.3, 55.5; IR (KBr pellet, cm^{-1}) 2952 (ν_{C-H}), 2890 (ν_{C-H}), 2835 (ν_{C-H}), 1324 (ν_{C-N}), 946 (ν_{C-O-C}); MS (EI) *m/e* 455 ($(M - 1)^+$), 457 ($(M + 1)^+$), calcd for $C_{23}H_{22}NBrO_4$ 456.3. Anal. Calcd for $C_{23}H_{22}NBrO_4$: C, 60.5; H, 4.9; N, 3.1; Br, 17.5. Found: C, 60.4; H, 4.8; N, 3.0; Br, 17.4.

(3-Bromo-4-(1,3-dioxolan-2-yl)phenyl)bis(4-methoxyphenyl)amine (728 mg, 1.59 mmol) was dissolved in a mixture of acetone (16 mL) and water (0.50 mL) containing *p*-toluenesulfonic acid (214 mg, 1.13 mmol) and refluxed for 3 h. After evaporation, the mixture was extracted with ether. The organic layer was successively washed with aqueous sodium hydrogen carbonate and aqueous saturated sodium chloride and then evaporated. The crude product was purified using a silica gel column with hexane/ethyl acetate (3/1) to give **7** as an orange solid (656 mg): yield 93%; mp 146 °C; ^{1}H NMR (500 MHz, $CDCl_3$; ppm) δ 10.08 (s, 1H), 7.68 (d, $J = 8.8$ Hz, 1H), 7.13−6.89 (m, 9H), 6.73 (dd, $J = 2.5, 8.9$ Hz, 1H), 3.84 (s, 6H); ^{13}C NMR (500 MHz, $CDCl_3$; ppm) δ 190.0, 157.7, 154.4, 138.0, 130.7, 129.0, 128.1, 124.4, 119.9, 115.6, 115.2, 55.4; IR (KBr pellet, cm^{-1}) 2955 (ν_{C-H}), 2929 (ν_{C-H}), 2908 (ν_{C-H}), 2836 (ν_{C-H}), 1677 ($\nu_{C=O}$), 1341 (ν_{C-N}); MS (EI) *m/e* 411 ($(M - 1)^+$), 413 ($(M + 1)^+$), calcd for $C_{21}H_{18}NBrO_3$ 412.3. Anal. Calcd for $C_{21}H_{18}NBrO_3$: C, 61.2; H, 4.4; N, 3.4; Br, 19.4. Found: C, 60.3; H, 4.2; N, 3.3; Br, 19.3.

4-[*N*,*N*-Bis(4-methoxyphenyl)amino]-2-bromostyrene (5a). To 0.344 mL of a dry THF solution of triphenylmethylphosphonium bromide (117 mg, 0.327 mmol) were dropwise added a 0.136 mL hexane solution of *n*-butyllithium (0.218 mmol) and a dry 0.30 mL THF solution of **7** (45.6 mg, 0.111 mmol), and the mixture was stirred at room temperature for 1 h. After evaporation, the crude product was extracted with diethyl ether, washed with brine, dried over anhydrous sodium sulfate, evaporated, and purified with a silica gel column with a hexane/ethyl acetate (20/1) to give 44.7 mg of **5a** as a pale-yellow viscous liquid: yield 98%; ^{1}H NMR (500 MHz, $CDCl_3$; ppm) δ 7.34 (d, $J = 8.9$ Hz, 1H), 7.06−6.21 (m, 11H), 5.54 (dd, $J = 1.2, 17.4$ Hz, 1H), 5.19 (dd, $J = 1.3, 11.1$ Hz, 1H), 3.82 (s, 6H); ^{13}C NMR (500 MHz, $CDCl_3$; ppm) δ 156.4, 149.3, 140.0, 135.2, 128.8, 127.0, 126.6, 124.1, 122.9, 118.9, 114.9, 113.7, 55.5; IR (KBr pellet, cm^{-1}) 2952 (ν_{C-H}), 2930 (ν_{C-H}), 2834 (ν_{C-H}), 1325 (ν_{C-N}); MS (EI) *m/e* 409 ($(M - 1)^+$), 411 ($(M + 1)^+$), calcd for $C_{22}H_{20}NBrO_2$ 410.3. Anal. Calcd for $C_{22}H_{20}NBrO_2$: C, 64.4; H, 4.9; N, 3.4; Br, 19.5. Found: C, 64.1; H, 5.0; N, 3.2; Br, 19.7.

4-[*N*,*N*-Bis(4-*tert*-butylphenyl)amino]-2-bromotoluene (8). To a 15 mL toluene solution of bis(4-*tert*-butylphenyl)amine (0.56 g, 2 mmol) were added 2-bromo-4-iodotoluene (0.59 g, 2.0 mmol), tris(dibenzylideneacetone)dipalladium (0.27 g, 0.30 mmol), tris(*o*-tolyl)phosphine (0.091 g, 0.30 mmol), and sodium *tert*-butoxide (0.58 g, 6.0 mmol), and the mixture was stirred for 15 h at 70 °C under nitrogen and then cooled to room temperature. The crude product was extracted with chloroform, washed with water, and dried over anhydrous magnesium sulfate. The solvent was removed in vacuo, and the residue was purified using a silica gel column with a hexane eluent and recrystallized from hexane to afford 0.47 g of **8** as white crystals: yield 52%; mp 133 °C; ^{1}H NMR (500 MHz, $CDCl_3$; ppm) δ 7.25−6.88 (m, 11H), 2.32 (s, 3H), 1.30 (s, 18H); ^{13}C NMR (500 MHz, $CDCl_3$; ppm) δ 147.2, 145.8, 144.8, 131.0, 130.9, 126.7, 126.1, 124.9, 123.7, 122.3, 34.3, 31.4, 22.1; IR (KBr pellet, cm^{-1}) 2956 (ν_{C-H}), 1267 (ν_{Br-C}), 1030 (ν_{C-N}); MS (EI) *m/e* 449 ($(M - 1)^+$), 451 ($(M + 1)^+$), calcd for $C_{27}H_{32}NBr$ for 450.5. Anal. Calcd for $C_{27}H_{32}NBr$: C, 72.0; H, 7.2; N, 3.1; Br, 17.7. Found: C, 71.8; H, 7.0; N, 3.0; Br, 17.6.

4-[*N*,*N*-Bis(4-*tert*-butylphenyl)amino]-2-bromostyrene (5b). *N*-Bromosuccinimide (1.8 g, 10.0 mmol) and a trace amount of azobisisobutyronitrile were added to a 50 mL tetrachloromethane solution of **8** (9.0 g, 20 mmol). The mixture was vigorously stirred at 60 °C for 3 h, filtered, and evaporated. The residue was dissolved in a 5 mL benzene solution of triphenylphosphine (2.6 g, 10 mmol) and stirred at 50 °C for 5 h. Evaporation gave a red oil, which was purified using a silica gel column with a hexane/chloroform (1/1) eluent to give a yellow oil as the corresponding phosphonium salt (5.4 g). The phosphonium salt (5.4 g, 6.8 mmol) was dissolved in 1.0 N aqueous formaldehyde (19 mL). A 2 N aqueous sodium hydroxide (3 mL) solution was added dropwise to the phosphonium salt solution, stirred for 3 h, and extracted with diethyl ether. The organic layer was washed with brine, dried over anhydrous sodium sulfate, and evaporated. The residue was purified using a silica gel column with a hexane eluent to give **5b** as an amorphous white solid (0.91 g): yield 29%; ^{1}H NMR (500 MHz, $CDCl_3$; ppm) δ 7.63−6.92 (m, 12H), 5.56 (d, $J = 18.4$ Hz, 1H), 5.21 (d, $J = 12.1$ Hz, 1H), 1.30 (s, 18H); ^{13}C NMR (500 MHz, $CDCl_3$; ppm) δ 148.8, 146.6, 144.2, 135.2, 130.0, 126.7, 126.2, 125.1, 124.5, 124.0, 121.1, 114.1, 34.4, 31.4; IR (KBr pellet, cm^{-1}) 3033 (ν_{C-H}), 2954 (ν_{C-H}), 1622 ($\nu_{C=C}$), 1267 (ν_{C-N}) cm^{-1}; MS (EI) *m/e* 461 ($(M - 1)^+$), 463 ($(M + 1)^+$), calcd for $C_{28}H_{32}BrN$ 462.5. Anal. Calcd for $C_{28}H_{32}NBr$: C, 72.7; H, 7.0; N, 3.0; Br, 17.3. Found: C, 72.5; H, 6.8; N, 2.9; Br, 17.5.

Polymerization. The polymerization was carried out by modifying the procedure described in the previous papers.[7,25] Palladium acetate, tris(*o*-tolylphosphine), triethylamine, and lithium chloride were added to the monomer **5** solution of DMF, and the mixture was heated (examples of the polymerization conditions are given in Table 3). The polymerization mixture was poured into methanol, and the precipitated polymer powder was purified by reprecipitation from chloroform into the mixture of methanol/benzene (3/7) to afford the polymer **1**.

Magnetic Measurements. The PF_6^- salt of $\mathbf{1}^+$ was isolated by pouring the methylene chloride solution of $\mathbf{1}^+$ oxidized with a small excess of $NOPF_6$/18-crown-6-ether into dimethyl ether (Anal. Calcd for $C_{22}H_{19}NF_6O_2P$: C, 55.7; H, 4.0; N, 3.0. Found: C, 55.3; H, 4.2; N, 2.9). Besides the neat sample, $\mathbf{1}^+$ was also isolated in the presence of polystyrene or poly(styrenesulfonate tetrabutylammonium) **4**. The neat sample was dissolved again in the methylene chloride solution of polystyrene or **4** ([polystyrene or **4**]/[$\mathbf{1}^+$] = 100 w/w), and the

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TABLE 3. Polymerization Conditions of 5 and 9[a]

run	monomer	$[M]_0$/mol/L	$[(C_2H_5)_3N]_0/[M]_0$	additive	T/°C	time/h	$M_w/10^3$	M_w/M_n	yield[b]/wt %
1	**5a**	0.1	2.0	none	100	24	1.7	1.3	22
2	**5a**	0.2	2.0	none	70	24	1.8	1.4	15
3	**5a**	0.5	1.2	none	100	24	2.4	1.3	40
4	**5a**	0.2	1.2	LiCl	70	72	4.3	1.3	69
5	**5a**	0.5	1.2	LiCl	100	24	4.2	1.3	37
6	**5b**	0.1	2.0	none	100	18	3.1	1.2	45
7	**5b**	0.2	1.2	LiCl	70	72	5.1	1.4	83
8	**9**	1.0	2.0	LiCl	100	24	2.7	1.3	55
9	**9**	0.2	1.2	LiCl	70	72	2.8	1.2	53
10	**9**	1.0	1.2	none	70	24	1.1	1.2	33
11	**9**	1.0	1.2	LiCl	70	24	2.0	1.4	42

[a] $[Pd(OAc)_2]/[M]_0 = 1/100$; $[P(o\text{-tolyl})_3]/[Pd(OAc)_2] = 4$; $[\text{additive}]/[M]_0 = 5$. [b] Methanol/benzene (7/3) insoluble part.

solvent was thoroughly removed to give a powder of the isolated sample. The neat and isolated samples were transferred to a diamagnetic plastic capsule after the oxidation. The magnetization and static magnetic susceptibility were measured with a Quantum Design MPMS-7 SQUID magnetometer. The magnetization was measured from 0.1 to 7 T at 1.8, 2.0, 2.5, 3.0, and 5.0 K. The static magnetic susceptibility was measured from 1.8 to 280 K in a 0.5 T field. The ferromagnetic magnetization ascribed to the impurities was determined by the Honda−Owen plots to be very low (< 1 ppm) and subtracted from the overall magnetization. The diamagnetic susceptibility of the diluent and capsule was estimated by the Curie plots of magnetic susceptibility. The corrected magnetization data was fitted to Brillouin functions using a self-consistent version of the mean field approximation.[3b]

Evans NMR Shift Measurement. The magnetic susceptibility of $\mathbf{1}^+$ was measured by the Evans NMR shift method.[23] The $\mathbf{1}^+$ $CDCl_3$ solution was prepared by the oxidation of **1** with a small excess of $NOPF_6$/18-crown-6-ether. An inner NMR tube (ϕ2 mm) was filled with the mixture of the $\mathbf{1}^+$ solution and cyclohexane, and placed in the center of an outer standard NMR tube (ϕ5 mm) which was filled with the mixture of $CDCl_3$ and cyclohexane. The NMR spectrum was recorded at 499.10 MHz. The peak shift, $\Delta\nu$, was estimated by frequency separation between those of the internal and the external cyclohexane peaks. The magnetic susceptibility was calculated by the linear relation between $\Delta\nu$ and sample concentrations.

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Supporting Information Available: Syntheses and characterization of 2-bromo-4-iodobenzaldehyde and ^{13}C-labeled 2-bromo-5-hexyloxystyrene; ESR spectrum of $\mathbf{3a}^+$; magnetic susceptibility data measured by the NMR shift method and other measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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