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Dendron-Combined Poly(4-diphenylaminium-1,2-phenylenevinylene): An Isolated Multiplet Molecule

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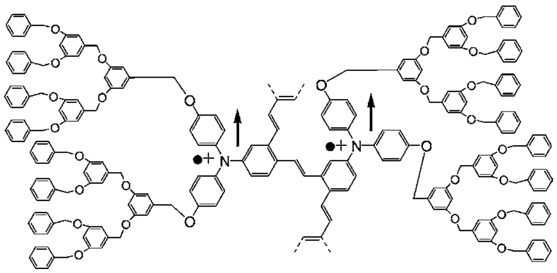
ABSTRACT



Poly[4-(*N*,*N*-bis(4-3,5-bis(3,5-bis(benzyloxy)benzyloxy)benzyloxyphenyl)amino)-1,2-phenylenevinylene] was prepared by the palladium-catalyzed polycondensation of the dendron-coupled bromostyrene and oxidized to yield the corresponding poly(aminium cationic radical): The dendron-combined polyradical molecule displayed both a substantial chemical stability and a multiplet state without any intermolecular interaction.

Much effort has been expended in synthesizing purely organic high-spin polyradical molecules that are predicted to display a molecular-based magnetism.[1] One of the approaches to ferromagnetically aligning the spins on radical groups focuses on a π-conjugated linear polymer backbone that has multiple pendant radical groups in a non-Kekulé and nondisjoint fashion.[2,3] On the basis of this design, we have synthesized poly[4-*N*,*N*-bis(4-methoxyphenylaminium)-1,2-phenylenevinylene] **1b**$^{+}$ by introducing a spin-delocalized arylaminium cation as the pendant radical.[4] The poly(cationic radical) displayed an average spin quantum number (S) of (4.5)/2 based on the through π-conjugated backbone or intramolecular ferromagnetic spin-exchange interaction. However, a through-space and antiferromagnetic interaction occurred between the high-spin molecules, which sacrificed the ferromagnetic behavior especially at low temperature. The through-space interaction had been partially reduced by diluting the high-spin molecule with diamagnetic solvents or polymers, but the dilution brought about a significant decrease in the content of the spin-active molecule in the sample. Dendrons, the subpart of dendrimers, possess a regular branchlike three-dimensional structure.[5] The dendron moiety has been designed, synthesized, and applied to cover and sterically isolate the core active site with its bulky structure.[6] For example, dendron-combined porphyrins and ferrocenes have been synthesized to examine the isolation of the redox-active core. In this study, we synthesized a

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(6) (a) Sadamoto, R.; Tomioka, N.; Aida, T. *J. Am. Chem. Soc.* **1996**, *118*, 3978. (b) Pollak, K. W.; Leon, J. W.; Fréchet, J. M.; Maskus, M.; Abruña, H. D. *Chem. Mater.* **1998**, *10*, 30. (c) Vögtle, F.; Plevoets, M.; Nieger, M.; Azzellini, G. C.; Credi, A.; De Cola, L.; De Marchis, V.; Venturi, M.; Balzani, V. *J. Am. Chem. Soc.* **1999**, *121*, 6290. (d) Stone, D. L.; Smith, D. K.; McGrail, P. T. *J. Am. Chem. Soc.* **2002**, *124*, 856.

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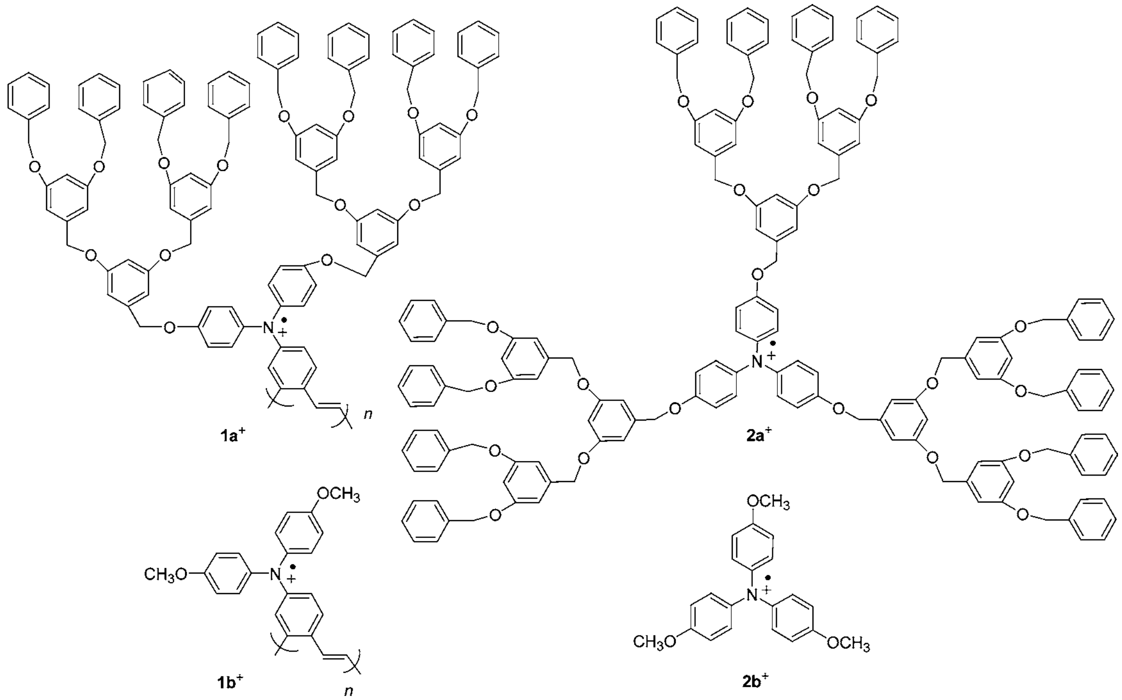
Chart 1

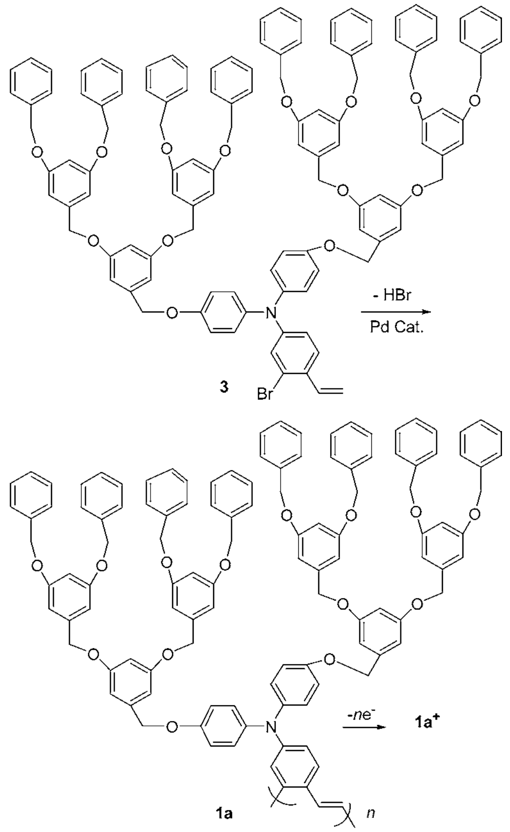


dendron-combined poly(4-diphenylaminium-1,2-phenylenevinylene) **1a**$^+$ with a well-defined chemical structure to suppress the through-space magnetic interaction of the high-spin molecule.

A head-to-tail-linked structure of the π-conjugated polyradical is essential for the non-Kekulé and nondisjoint requisite for the following magnetic study, which was established in this investigation through the polycondensation via the Pd-catalyzed Heck reaction of the 4-radical precursor-substituted 2-bromostyrene. The 3,5-bis(3,5-bis(benzyloxy)benzyloxy)-benzyloxy group was selected as the dendron moiety and prepared using a convergent approach via the Willianson reaction.[7] The dendron-coupled bromostyrene molecule, 4-(*N*,*N*-bis(4-3,5-bis(3,5-bis(benzyloxy)benzyloxy)benzyl-oxyphenyl)amino)-2-bromostyrene **3**, was synthesized as a monomer via the Pd-catalyzed cross-coupling reaction of bis-(4-(3,5-bis(3,5-bis(benzyloxy)benzyloxy)benzyloxy)phenyl)-amine and 2-(2-bromo-4-iodo-phenyl)-[1,3]dioxolane, and the following Wittig reaction (see Supporting Information).

3 was polymerized using the Pd-tri(*o*-tolyl)phosphine catalyst in the presence of triethylamine as a base in DMF solution at 70 °C for 1 week (Scheme 1).[4b] This polymerization condition was selected for the selective β-arylation of the vinyl group with the aryl bromide to avoid the formation of chemical defects such as the 1,1-diphenylethylene linkage derived from α-arylation. The brownish yellow polymer **1a** was soluble in the common solvents such as methylene chloride, benzene, and THF. The molecular weight of **1a** measured by GPC with a polystyrene standard was 7400, which almost agreed with the molecular weight of 7000 estimated by the terminal bromine content. The degrees of polymerization of **1a** and the nondendron-type **1b** po-

Scheme 1



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lymerized under the same conditions were 4.3 and 12.8, respectively; this is because the bulky dendron moiety retarded the Heck reaction between the vinyl group and the arylbromide. The polydispersity (the ratio of number- and weight-average molecular weight) was 1.2 and 1.3 for **1a** and **1b**, respectively.

The chloroform solution of **1a** showed UV absorption maxima at 284, 302, and 370 nm ($\epsilon = 2.4 \times 10^4$, 1.6×10^4, and 0.65×10^4 M^{-1} cm^{-1}, respectively), which were ascribed to the dendron moiety, the triphenylamine pendant, and the *trans*-stilbene backbone, respectively. The visible absorption was extended to 503 and 504 nm for **1a** and **1b**, respectively. The chloroform solution exhibited a yellowish green photoluminescence: The $\lambda_{em} = 507$ nm for **1a** with DP = 4.3 (the $\lambda_{em} = 506$ nm for **1b** with DP = 4.1) was bathochromically shifted in comparison with those for the monomeric amines, **2a** and **2b** (396 and 398 nm, respectively). The phenylenevinylene backbone maintains its π-conjugation, despite the bulky dendron introduction for **1a**.

Cyclic voltammograms for the oxidation of the polymers **1** and the monomeric amines **2** were reversibly recorded in the repeated potential sweeps at room temperature. The potential separations between the oxidation and reduction peaks ($\Delta E_p^{a-c} = E_p^a - E_p^c$) and the redox potential ($E_p^{1/2} = (E_p^a + E_p^c)/2$) are listed in Table 1. The redox wave for **1a** was broader than that of **1b**, and the potential separations ΔE_p^{a-c} for **1a** and **2a** were greater than those for **1b** and **2b**. This result is explained by the slower electron-transfer process for **1a** and **2a** that resulted from the amine moiety being covered by the bulky dendron. The anodic shift in the redox potential for the polymers **1** could be ascribed to the delocalization effect of the formed aminium cationic radical conjugated with the phenylenevinylene backbone and to the electrostatic repulsion influence of the cationic radicals.[8]

Table 1. Redox Potential ($E_p^{1/2}$) and Peak Separation (ΔE_p^{a-c}) of Polymers **1** and Monomeric Amines **2**[a]

	dendron-combined (**a**)		nondendron-type (**b**)	
amine	$E_p^{1/2}$ [V]	ΔE_p^{a-c} [V]	$E_p^{1/2}$ [V]	ΔE_p^{a-c} [V]
1	0.80	0.22	0.81	0.17
2	0.75	0.22	0.68	0.13

[a] Methylene chloride solution of 0.1 M $(C_4H_9)_4NBF_4$, vs Ag/AgCl (reference ferrocene Fc/Fc$^+$ = 0.58 V), sweep rate = 50 mV/s.

Triaryl aminium cationic radical salts, **1a**$^+$ and **1b**$^+$, were prepared by oxidizing the corresponding triarylamines **1** with the $NOBF_4$ or $NOPF_6$ salt solubilized with 18-crown-6-ether, by considering both the oxidation potential of **1** and the counteranion species.[9,10] The color of the methylene chloride solution of **1a** turned from pale yellow to deep blue,[11,12] which agreed with the UV/vis absorption change for **1b** ($\lambda_{max} = 301$ nm for **1b** and 756 nm for **1b**$^{+4}$). A deep blue colored powder of **1a**$^+$ was obtained, of which the spin concentration was estimated to be 0.78 spin/monomer amine unit.[13] The half-life (τ) of the aminium cation radical **1a**$^+$ in the powder state was 2 months at room temperature,[14] which was remarkably longer than that for **1b**$^+$ ($\tau = 11$ days). The dendron-covering significantly suppressed any chemical side reaction of the aminium cation radical in **1a**$^+$ and prolonged its half-life.

The ESR spectrum of **1a**$^+$ with a low spin concentration gave a three-line signal at $g = 2.0034$ and changed to a strong unimodal signal with the increasing spin concentration, indicating a local high spin concentration along the polymer backbone (see inset of Figure 1). The frozen glass of **1a**$^+$ gave a $\Delta M_s = \pm 2$ (half field and forbidden) transition at 160 mT, which is assigned to a triplet species. The signal intensity of the $\Delta M_s = \pm 2$ transition of **1a**$^+$ was proportional to the reciprocal of the temperature and followed Curie's law (Figure 1). This result indicates a triplet ground state with a large triplet−singlet energy gap (however, it does not rule out the possibility of a degenerate singlet−triplet state).

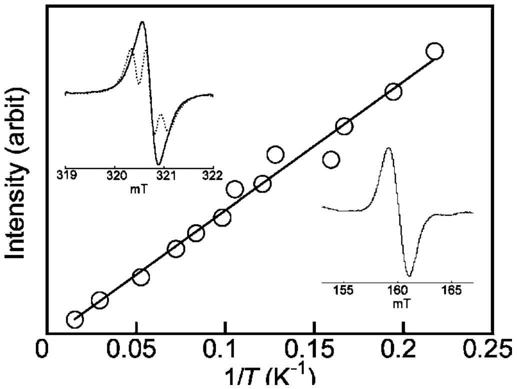

Figure 1. Temperature dependency of the ESR signal intensity of the $\Delta M_s = \pm 2$ transition of **1a**$^+$ with 0.78 spins/unit in methylene chloride. The solid line is a least-squares fitting to Curie's law (intensity = C/*T*). Inset: ESR spectra of the **1a**$^+$ methylene chloride solution with a low spin concentration of 0.10 spin/unit (dashed line) and a high spin concentration of 0.78 (solid line) at room temperature, and the $\Delta M_s \pm 2$ spectrum of **1a**$^+$ at 4.0 K.

The static magnetic susceptibility (χ) and magnetization (M) for the powder sample of **1**$^+$ were measured using a

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(12) Concentrated methylene chloride solution of $NOBF_4$ or $NOPF_6$ was added dropwise to the dilute methylene chloride solution of the amine polymer **1** to provide a high yield upon the aminium cationic radical formation. The PF_6^- salt of **1**$^+$ was isolated as a blue powder by pouring the methylene chloride solution of **1**$^+$ oxidized with $NOPF_6$ into diethyl ether. The precipitated powder was composed of the PF_6^- salt of **1**$^+$ on the basis of the elemental analysis.

(13) Measured by the ESR signal intensity.

(14) τ of **2a**$^+$ estimated by the ESR signal intensity was greater than 3 months.

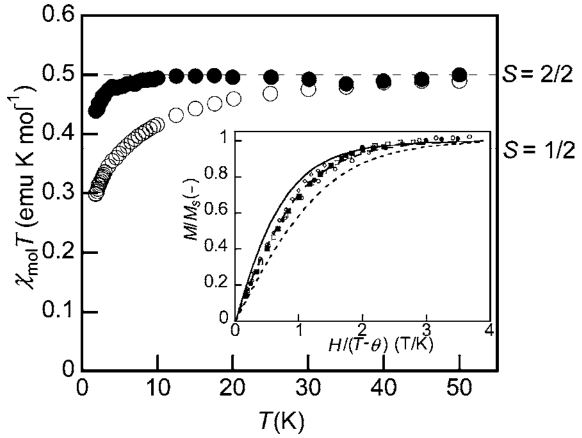

Figure 2. $\chi_{mol}T$ vs T plots for the powder sample of $\mathbf{1}^+$. (●): Powder neat sample of $\mathbf{1a}^+$ with a spin concentration of 0.68. (○): Powder neat sample of $\mathbf{1b}^+$ with a spin concentration of 0.65. Inset: Normalized plots of magnetization (M/M_s) vs the ratio of the magnetic field and temperature ($H/(T - \theta)$ for the neat powder $\mathbf{1a}^+$ at 1.8 (○), 2 (●), 2.5 (□), 3 (■), 5 (◇). Theoretical Brillouin curves for $S = 1/2$ (dashed line), 2/2 (broken line), and 3/2 (solid line).

SQUID magnetometer. χ was normalized to the χ_{mol} values using the radical or spin concentration in the sample determined by the saturation magnetization (M_s) of the M vs magnetic field (H) plots. Figure 2 shows the magnetic susceptibility plots ($\chi_{mol}T$) vs T plots for $\mathbf{1}^+$. The $\chi_{mol}T$ plots for the dendron-combined aminium polyradical $\mathbf{1a}^+$ were flat even at low temperature, although the plots for the nondendron-type $\mathbf{1b}^+$ decreased below 50 K. These results indicated that the antiferromagnetic and through-space interaction was suppressed by introducing the dendron moiety at the para position of the triphenylaminium radical.

The magnetization (M) normalized by the saturated magnetization (M_s), M/M_s, is represented by a Brillouin function. The M/M_s values of $\mathbf{1a}^+$ were plotted versus the effective temperature ($T - \theta$) and compared with the Brillouin curves where θ is the mean field parameter for the intermolecular magnetic interactions and was estimated by referring to the literature.[15] θ was estimated to be -0.08 K and -1.5 K, respectively, for the dendron-combined polyradical $\mathbf{1a}^+$ and the nondendron-type $\mathbf{1b}^+$, which supported the reduced intermolecular antiferromagnetic interaction. The bulky dendron moiety produced an isolated high-spin polyradical without any intermolecular interactions.

The normalized plots of magnetization (M/M_s) were close to the Brillouin curve for $S = 2/2$, indicating a triplet ground state for $\mathbf{1a}^+$ (see inset of Figure 2). Taking into account both the molecular weight or DP and the spin concentration of $\mathbf{1a}^+$, all radical spins in each polymer chain are considered to be aligned inside the dendron covering. S is expected to proportionally increase with the DP of the poly(aminium cationic radical) $\mathbf{1a}^+$, after optimizing the generation of the dendron or replacing other more flexible dendron species.

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Supporting Information Available: Syntheses and characterization of 4-(*N*,*N*-bis(4-3,5-bis(3,5-bis(benzyloxy)benzyloxy)benzyloxyphenyl)amino)-2-bromostyrene **3** and the polymer **1a**, measurement of the magnetic data, and cyclic voltammograns. This material is available free of charge via the Internet at http://pubs.acs.org.

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