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Poly(1,2-phenylenevinylene) Ferromagnetically 3,5-Bearing Phenoxyl Radicals

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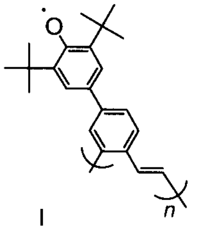
ABSTRACT: A π-conjugated but non-Kekulé- and nondisjoint-type molecule, poly(1,2-phenylenevinylene) 3,5-disubstituted with pendant phenoxyl radicals (**1a**), was designed as a new high-spin organic polymer and synthesized by the head-to-tail coupling polymerization of 2-bromo-3,5-bis(3,5-di-*tert*-butyl-4-aceotoxyphenyl)styrene (**3**) using a palladium catalyst. The corresponding high-spin dimer model compound bearing four phenoxyl radicals (**2a**) was also synthesized. The stepwise radical formation in **1** and **2** was electrochemically studied. The ESR signal at $\Delta M_s = \pm 2$ indicated a triplet ground state for **1** and **2**. However, the SQUID data revealed that the spin concentration and the average spin quantum number of **1a** and **2a** remained at ca. 0.5 spin/phenol unit and 2/2, respectively. A degradation at the vinylene bridge was suggested after the radical generation.

Introduction

In recent years, the design and synthesis of organic molecules with high-spin ground states have significantly increased, because the high-spin organic (macro)molecules are expected to develop new magnetically responsible organic materials.[1,2] π-Conjugated and alternant but non-Kekulé- and nondisjoint[3]-type molecules to realize the high-spin multiplet or ground states were first studied by synthesizing the polymers composed of *m*-phenylene-connected radicals in their main chains or cross-conjugated polyradicals.[4−6] For example, Rajca et al.[5b,c] demonstrated the highest-spin alignment (spin quantum number $S > 80/2$) by extending the cross-conjugated-type poly(1,3-phenylenephenylmethine) polyradicals to dendric−macrocyclic networks.

Another approach to synthesizing the high-spin polyradicals is based on a π-conjugated polymer bearing a pendant radical on each monomer unit which is substituted on the polymer main chain to satisfy the π-conjugated and alternant but non-Kekulé- and nondisjoint-type structure.[7−10] We have succeeded in and reported an intramacromolecular high-spin alignment with an average S of 2/2 ~ 10/2 by synthesizing poly(1,2-phenylenevinylene) (**I**)[7,8] and polythiophene[9] pendantly bearing a di-*tert*-butylphenoxyl at the 4- and 3-positions, respectively. The pendant-type high-spin polyradicals possess two advantages:[1a,7−9] first, substantial stability of the polyradical by introducing a chemically stable radical species, and second, reduced its sensitivity to the spin-defect damage for designing a high molecular size polyradical. The phenoxyl was an effective spin source of the pendant-type high-spin polyradical and displayed a well-balanced property with adequate chemical stability of the radical and a satisfactory spin-exchange interaction even in the presence of a spin defect.

However, there remained the following unsolved issue for our approach using pendant-type polyphenoxyl radicals. The spin-exchange or ferromagnetic interaction to align the pendant spins was not strong because of the longer distance between the neighboring radicals than those of the cross-conjugated polyradicals. This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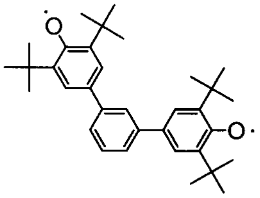
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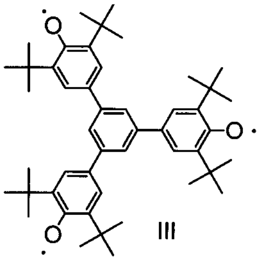
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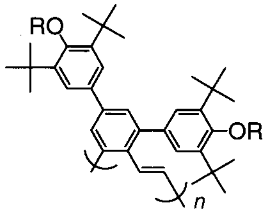
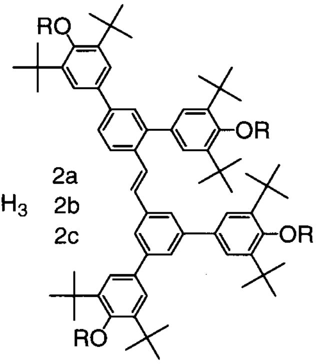
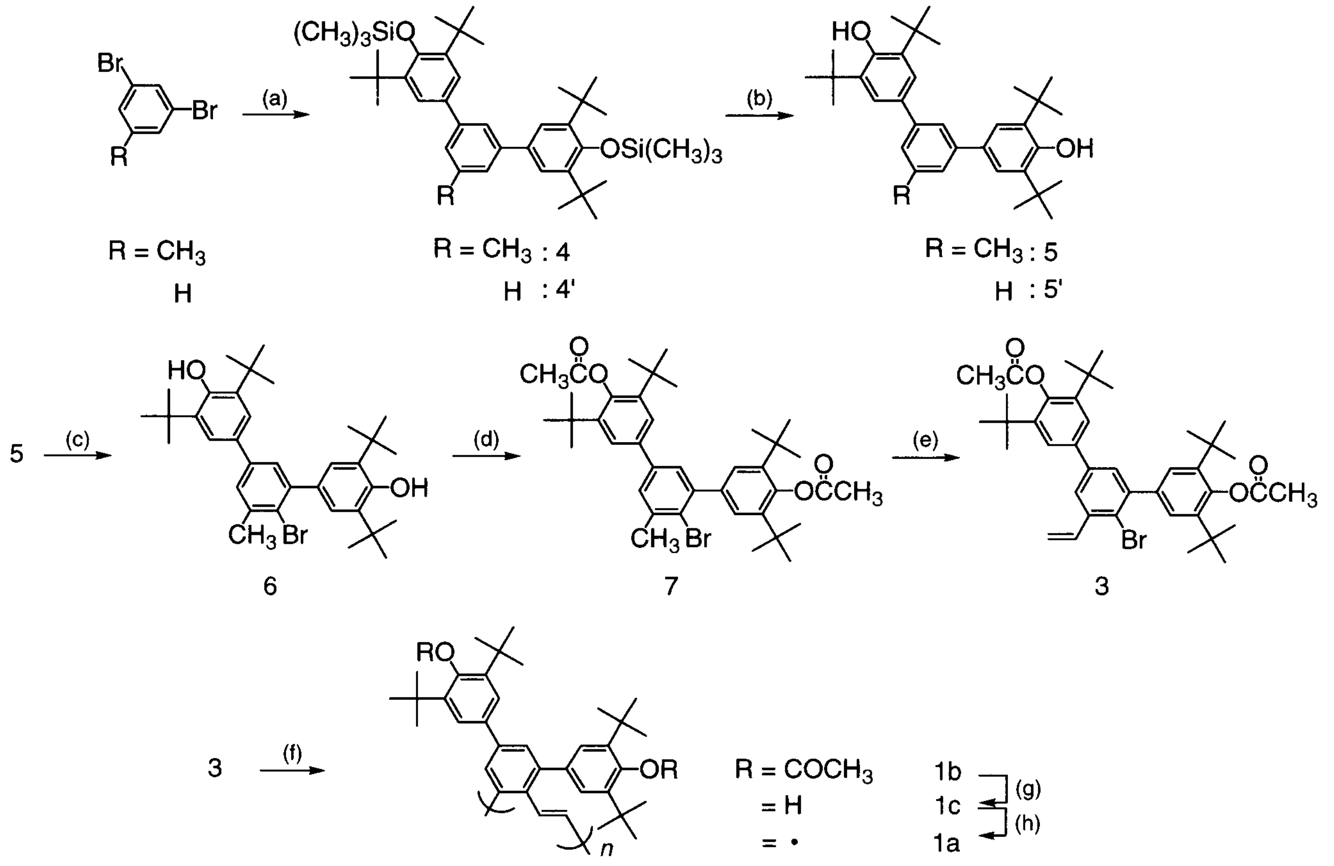

R = • 1a
= $COCH_3$ 1b
= H 1c


R = • 2a
= $COCH_3$ 2b
= H 2c

10.1021/ma011209f CCC: $22.00

Scheme 1[a]



[a] Reagent (a) 2,6-di-*tert*-butyltrimethylsiloxybenzene, Ni(dppp)Cl_2, THF; (b) HCl, THF/CH_3OH; (c) Br_2, Fe (cat.), $CHCl_3$; (d) $(CH_3CO)_2O$, $HClO_4$; (e) i; *N*-bromosuccine imide, AIBN, CCl_4, ii; triphenylphosphine, benzene, iii; NaOH(aq), HCHO; (f) Pd$(OAc)_2$, P(*o*-tolyl)$_3$, DMF, TEA; (g) KOH(aq), DMSO; (h) i: NaOH(aq), ii: K_3FeCN_6(aq).

paper describes our trials to overcome this issue by designing and synthesizing a new pendant-type polyradical bearing triplet biradical species on each monomer unit which is expected to significantly enhance the interaction between the neighboring (and even remote) pendant spins. In a previous paper,[11] we reported a very strong ferromagnetic interaction in and the triplet and quartet ground state of the *m*-phenylene-coupled bisphenoxyl and trisphenoxyl, *m*-bis(3,5-di-*tert*-butyl-4-phenoxyl)benzene (**II**) and 1,3,5-tris(3,5-di-*tert*-butyl-4-phenoxyl)benzene (**III**), respectively. This suggested that the *m*-phenylene acts as a strong ferromagnetic coupler in an extended polyradical bearing a triplet biradical. On the basis of the above-mentioned designing, we now describe the synthesis and characterization of the poly(1,2-phenylenevinylene) pendantly 3,5- (or *m*-) bearing triplet bisphenoxyls which satisfies the non-Kekulé- and nondisjoint-type ferromagnetic connectivity.

Table 1. Example of Polymerization and Molecular Weight[b] **of the Polymer**

run	monomer[a] concn (mM)	temp (°C)	time (h)	yield (%)	M_n [b]/10^3	M_w/M_n [b]
1	0.30	100	200	55	2.5	1.2
2	0.30	100	24	60	2.0	1.2
3	0.30	70	500	63	2.2	1.2
4	0.60	100	24	50	2.1	1.2

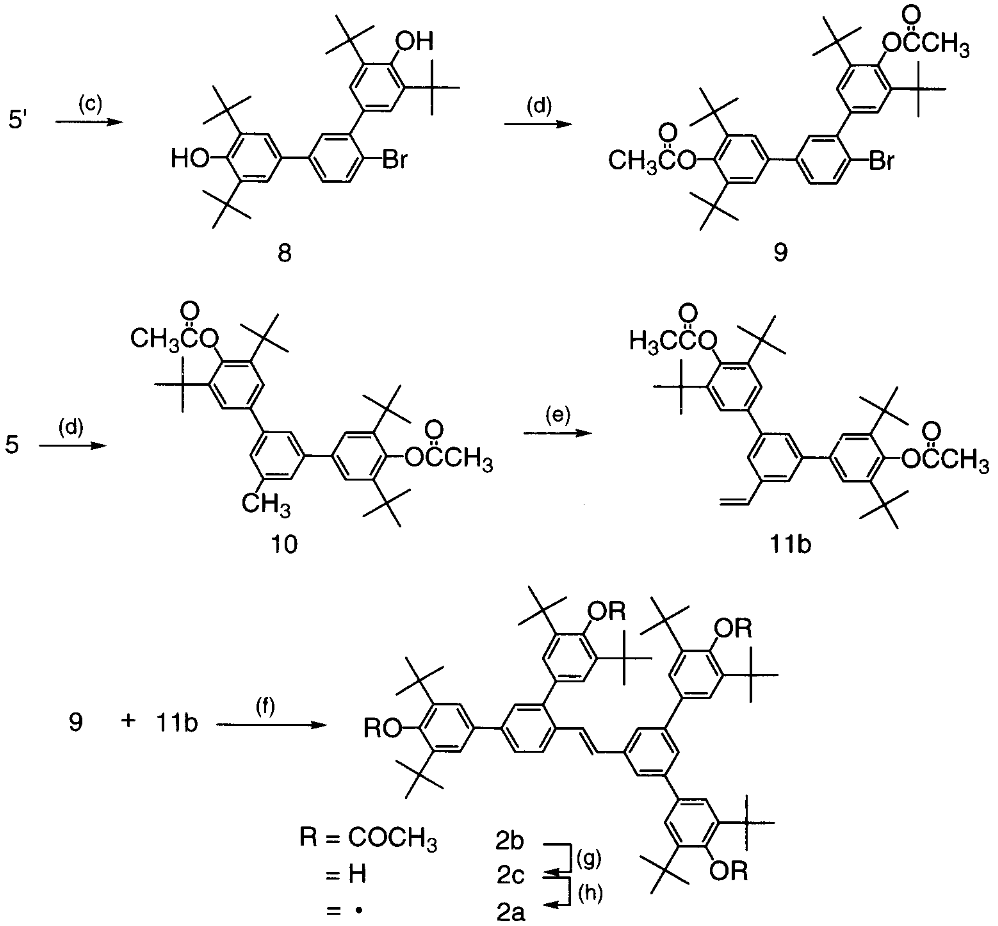
[a] $[Pd(OAc)_2]/[M]_0$ = 1/10, $[P(C_6H_4CH_3)_3]/[Pd(OAc)_2]$ = 2, $[N(C_2H_5)_3]/[M]_0$ = 5. [b] Number- and weight-average molecular weight measured by GPC.

Results and Discussion

Syntheses of Poly- and Tetraradical Precursors. A restricted primary structure or complete head-to-tail linkage in a poly(3,5-bis-substituted-1,2-phenylenevinylene) precursor is absolutely necessary to realize the ferromagnetic connectivity in the subsequently formed polyradical. We selected the reductive polycondensation of 2-bromo-3,5-disubstituted styrene via the Heck reaction catalyzed by a palladium−phosphine complex. Because of poor yields in the preparation of 2-bromo-3,5-diiodotoluene, 3,5-dibromotoluene was used as the starting compound. 3,5-Dibromotoluene was reacted with (3,5-di-*tert*-butyl-4-(trimethylsiloxy)phenyl)magnesium bromide using a nickel catalyst to give 2-bromo-3,5-bis(3,5-di-*tert*-butyl-4-trimethylsiloxyphenyl)toluene and 3,5-bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)toluene (**5**) after deprotection, as shown in Scheme 1. **5** was successfully brominated using a small amount of iron powder. On this bromination, the TMS-protected **4** (**4′**) did not give the purposed product; the electron-donating phenol groups in **5** probably promoted the reaction. **5** (**5′**) was protected with an acetyl group, and the methyl group of **6** was converted to a vinyl group via the Wittig reaction to yield the bromostyrene monomer **3**, 2-bromo-3,5-bis(3,5-di-*tert*-butyl-4-aceotoxyphenyl)styrene.

3 was polymerized via the Heck reaction using a palladium−tri(*o*-tolylphosphine) complex (Table 1). The product was obtained as a pale yellow powder that was soluble in the common solvents such as benzene, THF, and chloroform, and its molecular weight was estimated to be 2.5 × 10^3 (degree of polymerization (DP) or n in **1b** = 4) with M_w/M_n = 1.2. The bromide content of the product determined by elemental analysis was lower

Scheme 2[a]



[a] Reagent (a) 2,6-di-*tert*-butyltrimethylsiloxybenzene, Ni(dppp)Cl_2, THF; (b) HCl, THF/CH_3OH; (c) Br_2, Fe (cat.), $CHCl_3$; (d) $(CH_3CO)_2O$, $HClO_4$; (e) i: *N*-bromosuccine imide, AIBN, CCl_4, ii: triphenylphosphine, benzene, iii: NaOH(aq), HCHO; (f) Pd$(OAc)_2$, P(*o*-tolyl)$_3$, DMF, TEA (g) KOH(aq), DMSO; (h) i: NaOH(aq), ii: K_3FeCN_6(aq).

than that based on the **1b** with DP = 4 (3% less). FAB-mass of the product indicated the formation of cyclic products ($n = 5-7$), although they could not be isolated. The CVFF force field calculation for **1b** suggested a steric hindrance of the 3,5-disubstituted groups during the polymerization.[12] The acetyl-protected polymeric derivatives **1b** were converted to the corresponding hydroxy derivative **1c** after complete elimination of the protecting acetyl group in alkaline solution.

The tetraradical precursor or the dimer model, 2,4,3′,5′-tetrakis(3,5-di-*tert*-butyl-4-acetoxyphenyl)stilbene (**2b**), was synthesized as shown in Scheme 2. Selective bromination of 3,5-bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)benzene (**5′**) gave **8**, which was converted to **9** with acetyl protection. On the other hand, the methyl group of **10** (the acetyl-protected **5**) was modified to a vinyl group via the Wittig reaction to yield 3,5-bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)styrene (**11**). **9** and **11** were coupled via the palladium-catalyzed Heck reaction to yield **2b**, which was converted to **2c**. The head-to-tail-linked dimer structure of **2c** was supported by the $^1H-^1H$ COSY spectrum (Figure 1).

UV−vis absorption (λ_{max}) of **3**, **2b**, and **1b** in chloroform solutions were 254, 326 ($\lambda_{shoulder} = 376$), and 303 nm ($\lambda_{shoulder} = 396$ nm), respectively. The absorption of the polymer **1b** extended to 500 nm. Despite its bulky substituents, **1b** maintained a π-conjugation. The emission spectra ($\lambda_{ex} = 300$ nm) of **1b** and **2b** were given at $\lambda_{em} = 448$ nm, which was ascribed to the *trans*-stilbene structure in the main chain.

Polyradical Formation and Its ESR Spectra. The poly- and tetraphenoxyl radicals **1a** and **2a** were prepared by heterogeneously treating the toluene solutions of the hydroxy precursors **1c** and **2c**, respectively, with a fresh lead dioxide powder or with an aqueous alkaline ferricyanide solution. The organic layer turned from green to dark purple for **1a** and **2a** after the oxidation. Formation of the phenoxyl radical was supported by the appearance of a new visible absorption at ca. 580 nm and the ESR signal at $g = 2.004_5$. The ESR spectrum of the model phenoxyl radical **11a** (the monoradical with a low spin concentration) derived from the hydroxy derivative (**11c**) of **11b** showed a hyperfine structure attributed to the phenyl and styrene protons (Figure 2a). This suggests an efficient spin density distribution through the entire molecule and the monomer structure would act as an effective ferromagnetic spin coupler.

The ESR spectra of **1a** and **2a** changed to sharp and unimodal signals with increasing spin concentration, indicating a locally high spin concentration along the polymer chain (Figure 2b). A frozen toluene glass of 15 mM **2a** with a spin concentration of 0.57 spin/phenol unit showed a $\Delta M_s = \pm 2$ forbidden transition; the ESR absorption at $g = 4$ is ascribed to a triplet species (inset in Figure 3). The temperature-dependent ESR experiment of **1a** and **2a** gave a linear relation for the doubly integrated ESR intensity of the $\Delta M_s = \pm 2$ signal as a function of the reciprocal temperature ($1/T$) at higher temperatures (>10 K), which was consistent with Curie's law (Figure 3). However, the plots substantially

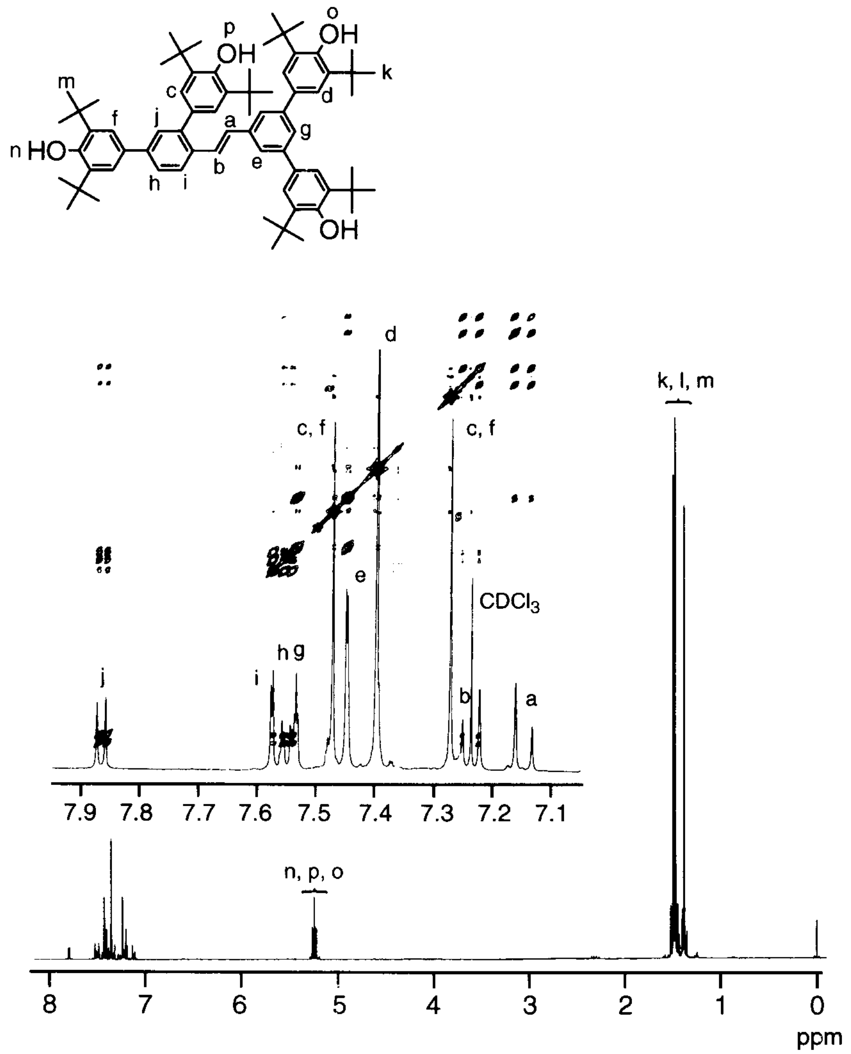


Figure 1. ^{1}H NMR spectrum of **2b**. Inset: ^{1}H$-^1$H COSY correlation in the aromatic region.

deviated upward from the linearity in the lower temperature region (<10 K). This upward deviation suggests a ferromagnetic interaction between the triplet species.

The phenoxyl radical was also generated by an electrochemical oxidation.We have reported that the *m*-phenylene-linked diphenolate anion (the oxidation form **II**) displayed two reversible redox waves in the cyclic and differential pulse voltammetries, which corresponded to the formation of the radical anion and the biradical.[11] The cyclic and differential pulse voltammograms of **2c** revealed similar two-wave profiles, as shown in Figure 4. It was considered that the two phenolates at the 2,3′- or 4,3′-positions of the stilbene backbone were first oxidized at the same time, and then the other phenolates were oxidized. The potential difference between the two redox waves for **2** (ca. 100 mV) was smaller than that of **II** (150 mV[11]). This means that the interaction between the two redox sites through the *m*-phenylene conjugation is weakened for **2** in comparison with the simple **II**, probably because of the steric hindrance in **2**. On the other hand, **1c** recorded under the same conditions gave a reversible but simple redox wave.

Coulometric oxidation of the phenolate anion derivatives from **1c** and **2c** on a carbon felt electrode indicated almost stoichiometric oxidation (Figure 5). The total number of electrons transferred per molecule (Q)[13] was close to the theoretical value of the phenol unit (ca. 92% for **2c**); all the potential spin sites could be oxidized to yield the poly- and tetraphenoxyl radicals.

Magnetic Properties. The magnetization (M) and static magnetic susceptibility (χ) of **1a** and **2a** in frozen toluene or 2Me-THF were measured using a SQUID magnetometer in order to estimate the intramacromolecular spin alignment between the pendant phenoxyl radicals through the phenylenevinylene or stilbene π-conjugation. The magnetization normalized with saturated magnetization, M/M_S, is plotted vs the effective temperature ($T - \theta$), where θ is the coefficient of a weak antiferromagnetic interaction between radicals (determined from curve fitting using the following $\chi_{\mathrm{mol}}T$ vs T data). The plots for the tetraradical **2a** with a spin concentration of 0.48 spin/phenol unit were close to the Brillouin curve for $S = 2/2$ at low temperature (Figure 6), indicating a ferromagnetic but two-spin alignment (triplet) at the ground state. The product of the molar magnetic susceptibility ($\chi_{\mathrm{mol}}T$) and T for **2a** approached the theoretical value ($\chi_{\mathrm{mol}}T = 0.50$ emu K mol^{-1}) for $S = 2/2$, as shown in the inset of Figure 6. The $\chi_{\mathrm{mol}}T$ plots were flat even at relatively high temperatures, which suggest a strong ferromagnetic interaction between the phenoxyl's spins. These results agree with those for the triplet biradical **II**.[11] The spin-exchange coupling constant (J) of the intramolecular spin alignment (or a force to align spins) through the π-conjugation was estimated

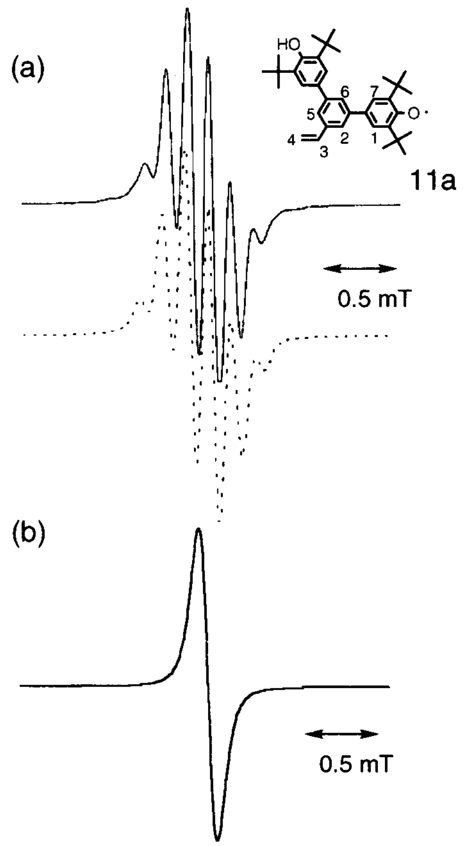


Figure 2. ESR spectra of the radicals at room temperature. (a) The model phenoxyl monoradical **11a** in 0.5 M toluene solution. The solid line is for the radical with spin concentration = 0.20 spin/phenol unit, and the dashed line is for the simulation with the following hyperfine coupling constants, a_H = 0.18 mT (1, 7 protons of the radical), 0.16 (2, 5, 6), 0.07 (3), and 0.05 (4), respectively. (b) **1a** with spin concentration = 0.48.

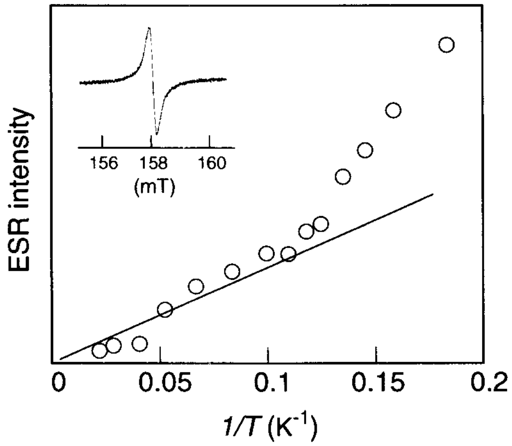


Figure 3. Temperature dependence of the $\Delta M_s = \pm 2$ ESR signal intensity for **2a** in toluene glass (inset, $\Delta M_s = \pm 2$ spectrum).

by curve fitting the $\chi_{mol}T$ data to the equation derived from the van Vleck expression for a linear three-spin system.[14,15] A large $2J$ value (ca. 160 cm^{-1}) was estimated from the parameters given in the footnote of Figure 6.

The M/M_s plots for **1a** with a spin concentration of 0.43 spin/phenol unit also lay on the Brillouin curve for $S = 2/2$ at 2−10 K, also indicating a triplet ground state for **1**. The $\chi_{mol}T$ plots were nearly similar to those of **2a**. These results concluded that the spin alignment in both **1a** and **2a** were attributed to the interaction of the *m*-phenylene connected biradical species but not through the vinylene bridge.

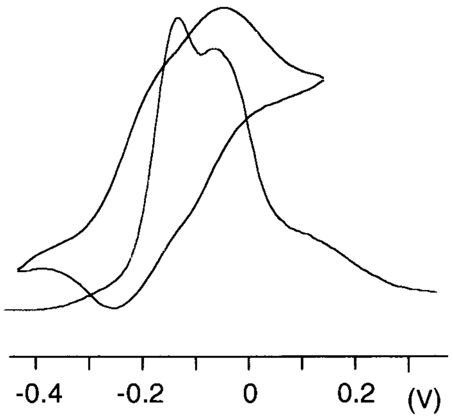


Figure 4. (a) Cyclic and differential pulse voltammograms for a 0.25 mM solution of **2c** in dichloromethane containing 0.1 M tetrabutylammonium tetrafluoroborate and tetrabutylammonium hydroxide. Cyclic voltammetry: scan rate = 100 mV/s. Differential pulse voltammetry: scan rate = 1 mV/s, pulse amplitude = 50 mV, width = 5 ms.

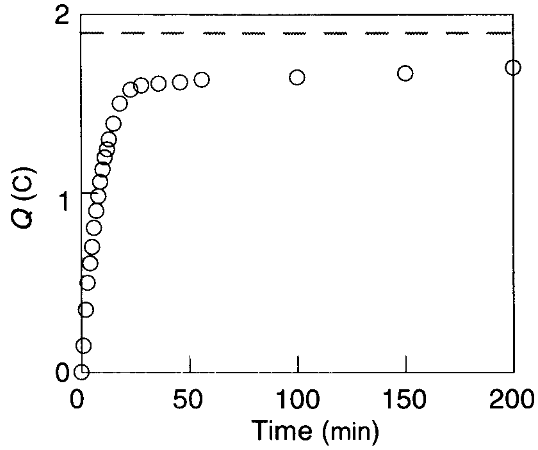


Figure 5. Controlled potential (0.2 V) coulometric oxidation of **2c** in dichloromethane solution containing 0.1 M tetrabutylammonium tetrafluoroborate and tetrabutylammonium hydroxide. The dashed line is for the theoretical value of 1.93 C.

During the radical preparation by chemical oxidation, we could not achieve a high radical yield for both **1a** and **2a**; all of the spin concentration values remained at 50−60% of the potential spin sites or the phenol unit (best result was 57%), which were independently estimated three ways, i.e., the saturated magnetization, the slope of χ vs $1/T$ plots, and the ESR intensity standardized with TEMPO, although the Coulometric oxidation established almost a stoichiometric radical generation. We now consider that the poly- and tetraradicals **1a** and **2a**, derived from the precursors **1c** and **2c**, respectively, are not chemically stable with time, e.g., for the magnetic measurement. To study the chemical stability of the stilbene-based and *m*-phenylene-connected bisphenoxyl radicals, **12b** and **13b** were prepared (Chart 1). The radical **12a** derived from **12b** was chemically unstable, but **13a** was relatively stable (half-life in the toluene solution was 1.2 days). In addition, one of the redox waves of **2** (at the higher potential) disappeared with time of over 10 min in the cyclic voltammetry shown in Figure 4. It is assumed that the spin density of the

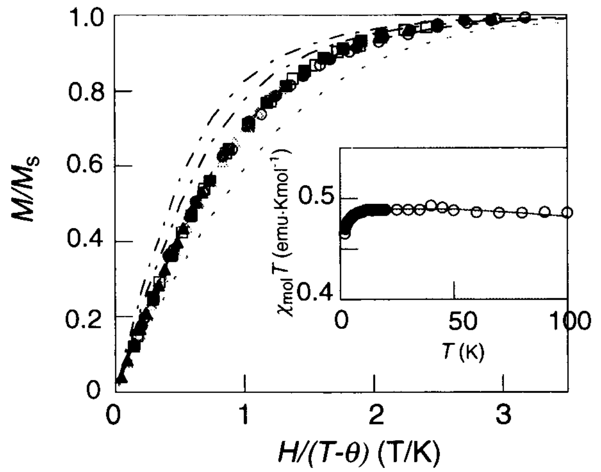
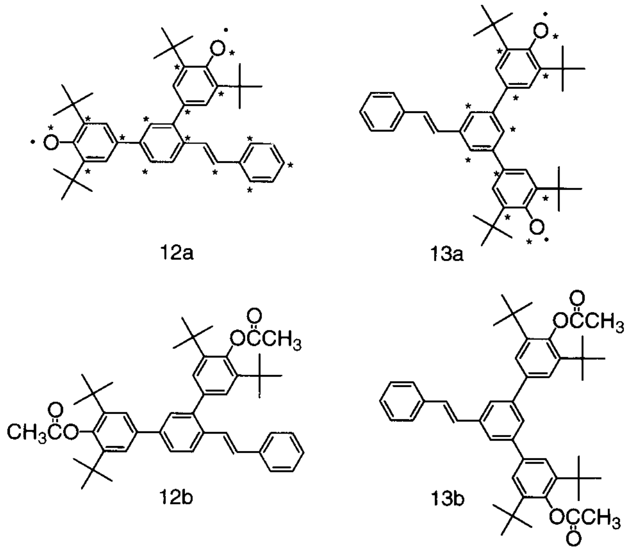


Figure 6. Normalized plots of magnetization (M/M_s) vs the ratio of magnetic field and temperature ($H/(T - \theta)$) for the tetraradical **2a** with spin concentration = 0.48 spin/phenol unit in toluene at $T = 1.8$ (○), 2.0 (●), 2.5 (□), 3 (■), 5(△), and 10 (▲) K and the theoretical curves corresponding to the $S = {}^1/_2$, ${}^2/_2$, ${}^3/_2$, and ${}^4/_2$ Brillouin functions. Inset: the $\chi_{mol}T$ vs T plots of **2** (○) (the solid line is the theoretical curve calculated using the equation in refs 14 and 15 with $2J = 160$ cm^{-1}, $\theta = -0.12$ K, $x_1 = 0.47$, $x_2 = 0.53$, and $x_3 = 0$).

Chart 1



12a 13a

12b 13b

unpaired electrons of the *o,p*′-substituted phenyl radicals in **12a** are delocalized through the vinylene bridge, where it becomes very reactive (as indicated with asterisks in Chart 1). A side chemical reaction is presumed for **12**, and **1a** and **2a**, to degrade the vinylene bridge or the π-conjugation to connect the triplet pendant radical species.

We could not achieve a high-spin alignment in both **1a** and **2a**, although the ferromagnetic interaction through the *m*-phenylene moiety worked effectively. The spin concentration remained less than 60%, because the formed polyradicals were chemically labile on the vinylene bridge of stilbene and the 1,2-phenylenevinylene main chain. To overcome this problem, an ethynylene bridge is considered to be more suitable than those of the vinylene and stilbene structures, because it is a hydrogen-free structure. Poly(1,2-phenylene−ethynylene) 3,5-bearing phenoxyls, instead of the vinylene derivative described in this paper, is expected to realize a very high-spin alignment through the π-conjugated main chain.

Experimental Section

3,5-Bis(3,5-di-*tert*-butyl-4-trimethylsiloxyphenyl)toluene (4). (4-Bromo-2,6-di-*tert*-butylphenoxy)trimethylsilane (85.8 g, 240 mmol) and dry THF (107 mL) were added to dry magnesium (5.8 g, 240 mol) under a nitrogen atmosphere. The mixture was stirred and refluxed until the magnesium completely reacted. The formed Grignard reagent was cooled to room temperature and diluted with dry THF (107 mL). It was added in portions, with stirring, to a dry THF (195 mL) solution of 3,5-dibromotoluene (17.5 g, 70 mmol) with dichloro-[1,3-bis(diphenylphosphino)propane]nickel(II) (0.12 g, 0.24 mmol) annealed in an ice bath for 0.5 h. The mixture was stirred at room temperature for 18 h, then treated with aqueous 2 N HCl (125 mL), extracted with ether, and washed with aqueous sodium bicarbonate and water. The ether layer was dried over anhydrous sodium sulfate. After evaporation, the crude product was recrystallized from ethanol to give 3,5-bis(3,5-di-*tert*-butyl-4-trimethylsiloxyphenyl)toluene: yield 41%; mp 222−223 °C. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm): δ 0.4 (s, 18H, $-Si(CH_3)_3$), 1.5 (s, 36H, *tert*-butyl), 2.5 (s, 3H, $-CH_3$), 7.3−7.5 (m, 7H, phenyl). ^{13}C NMR (CDCl$_3$, ppm): δ 17.7, 27.3, 31.3, 119.0, 120.8, 122.1, 129.3, 134.5, 136.9, 138.3, 148.8. IR (KBr pellet, cm^{-1}): 1257 (ν_{Si-C}), 914 (ν_{Si-O}). MS (*m*/*z*) 645 (M$^+$), calcd for M = 645.1.

3,5-Bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)toluene (5). 3,5-Bis(3,5-di-*tert*-butyl-4-trimethylsiloxyphenyl)toluene (4.6 g, 7.1 mmol) was dissolved in THF (40 mL), and methanol (26 mL) was added to this solution. The solution was acidified with aqueous 10 N HCl (10 mL) under a nitrogen atmosphere. After stirring for 3 h, the mixture was evaporated to remove methanol, extracted with ether, and washed with water. The ether layer was dried over anhydrous sodium sulfate and evaporated. The crude product was recrystallized from hexane to give white crystals: yield 79%; mp 224−225 °C. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm): δ 1.5 (s, 36H, *tert*-butyl), 2.5 (s, 3H, $-CH_3$), 5.3 (s, 2H, $-OH$), 7.2−7.5 (m, 7H, phenyl). ^{13}C NMR (CDCl$_3$, ppm): 30.4, 34.5, 123.3, 24.2, 126.2, 132.9, 136.1, 138.3, 142.8, 153.5. IR (KBr pellet, cm^{-1}): 3641 (ν_{O-H}). MS (*m*/*z*) 501 (M$^+$), calcd for M = 500.8.

2-Bromo-3,5-Bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)toluene (6). 3,5-Bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)toluene (2.1 g, 4.2 mmol) was dissolved in chloroform (200 mL), and a small amount of iron as a catalyst and bromine (0.8 g, 5.0 mmol) were added to this solution. The reaction was monitored by TLC and took for 24 h at room temperature. The mixture was extracted with chloroform and washed with water. The chloroform layer was dried over anhydrous sodium sulfate and evaporated. The crude product was purified by silica gel column separation with a hexane/CHCl$_3$ (4/1) eluent to give a white powder. It was recrystallized from hexane to give white crystals: yield 83%; mp 119−120 °C. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm): δ 1.5 (s, 36H, *tert*-butyl), 2.5 (s, 3H, $-CH_3$), 7.2−7.5 (m, 7H, phenyl). ^{13}C NMR (CDCl$_3$, ppm): δ 24.6, 31.1, 34.4, 34.5, 124.0, 126.6, 127.5, 127.8, 131.6, 133.1, 135.1, 136.3, 138.9, 140.9, 144.0, 153.2, 153.7. IR (KBr pellet, cm^{-1}): 3638 ($\nu_{C=O}$). MS (*m*/*z*) 578, 580 (M$^+$, M$^+$ + 2), calcd for M = 579.7.

2-Bromo-3,5-bis(3,5-di-*tert*-butyl-4-aceotoxyphenyl)toluene (7). A few drops of perchloric acid were added to 2-bromo-3,5-bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)toluene (2.0 g, 3.4 mmmol) suspended in acetic anhydride (30 mL). After stirring for 15 h, unreacted acetic anhydride was hydrolyzed by adding excess water. The mixture was extracted with ether and washed with water. The ether layer was dried over anhydrous sodium sulfate and evaporated. The crude product was recrystallized from hexane to give white crystals: yield 79%; mp 106−107 °C. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm): δ 1.4 (s, 36H, *tert*-butyl), 2.4 (s, 6H, $-CH_3$), 2.6 (s, 3H, $-O-CO-CH_3$), 7.3−7.5 (m, 6H, phenyl). ^{13}C NMR (CDCl$_3$, ppm): δ 19.0, 31.5, 35.6, 125.5, 127.9, 128.0, 128.5, 131.2, 138.5, 139.1, 139.2, 140.4, 141.7, 142.9, 143.5, 147.2, 147.7, 171.1. IR (KBr pellet, cm^{-1}): 1760 ($\nu_{C=O}$). MS (*m*/*z*): 662, 664 (M$^+$, M$^+$ + 2), calcd for M = 663.7.

3,5-Bis(3,5-di-*tert*-butyl-4-aceotoxyphenyl)toluene (10). **10** was prepared in the same manner of **7** using **5**, to give white crystals: yield 96%; mp 219−220 °C. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm): δ 1.4 (s, 36H, *tert*-butyl), 2.4 (s, 3H, −CH$_3$), 2.5 (s, 3H, −CH$_3$), 5.3 (s, 2H, −OH), 7.2−7.5 (m, 7H, phenyl). ^{13}C NMR (CDCl$_3$, ppm): 22.7, 31.5, 35.6, 124.1, 125.7, 127.0, 138.4, 138.6, 142.3, 142.6, 147.5, 171.2. IR (KBr pellet, cm^{-1}): 1762 ($\nu_{C=O}$). MS (*m*/*z*): 585 (M$^+$), calcd for M = 584.8.

3,5-Bis(3,5-di-*tert*-butyl-4-aceotoxyphenyl)styrene (11b). **11b** was prepared in the same manner of **3** using **10**, to give white crystals: yield 80%; mp 219−220 °C. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm): δ 1.4 (s, 36H, *tert*-butyl), 2.4 (s, 3H, −CH$_3$), 5.3 (d, 1H, 11 Hz, −CH═C**H**$_2$), 5.9 (d, 1H, 17 Hz, −CH═C**H**$_2$), 6.86 (dd, 1H, 11 Hz, 17 Hz, −C**H**═CH$_2$), 7.52 (d, 2H, phenyl), 7.54 (s, 4H, phenyl), 7.58 (t, 1H, phenyl). ^{13}C NMR (CDCl$_3$, ppm): 22.7, 31.5, 35.6, 114.5, 124.1, 125.6, 126.5, 136.8, 138.2, 142.6, 147.6, 171.2. IR (KBr pellet, cm^{-1}): 1764 ($\nu_{C=O}$), 1632 ($\nu_{C=C}$). MS (*m*/*z*): 597 (M$^+$), calcd for M = 596.8.

3,5-Bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)styrene (11c). **11b** was dissolved in a slight amount of THF. To its suspension in DMSO was added 2.5 N KOH under a nitrogen atmosphere. The solution was stirred at 40−50 °C for 15 h, cooled to room temperature, and neutralized with 1 N HCl. The organic product was extracted with CHCl$_3$, and the organic layer was evaporated and the crude product was recrystallized from hexane to give white crystals: yield 88%; mp 212−213 °C. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm): δ 1.4 (s, 18H, *tert*-butyl), 2.4 (s, 1H, OH), 5.4 (d, 1H, 11 Hz, −CH═C**H**$_2$), 5.9 (d, 1H, 17 Hz, −CH═C**H**$_2$), 6.88 (dd, 1H, 11 Hz, 17 Hz, −C**H**═CH$_2$), 7.16 (s, 4H, phenyl), 7.42 (s, 2H, phenyl), 7.58 (t, 1H, phenyl). ^{13}C NMR (CDCl$_3$, ppm): 22.8, 31.5, 113.8, 121.8, 124.1, 125.9, 128.0, 134.1, 135.7, 138.1, 142.2, 153.4. IR (KBr pellet, cm^{-1}): 3635 (ν_{O-H}), 1630 ($\nu_{C=C}$). MS (*m*/*z*): 513 (M$^+$), calcd for M = 512.8.

m-Bis(3,5-di-*tert*-butyl-4-trimethylsiloxyphenyl)benzene (**4′**) and *m*-bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)benzene (**5′**) were prepared as in the literature.[11]

1-Bromo-2,4-bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)benzene (8). **8** was prepared in the same manner of **6** to give white crystals: yield 85%; mp 224−225 °C. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm): δ 1.5 (s, 36H, *tert*-butyl), 2.2 (s, 3H, −CH$_3$), 5.3 (s, 1H, −OH), 7.3−7.5 (m, 7H, phenyl). ^{13}C NMR (CDCl$_3$, ppm): 30.3, 34.5, 121.0, 123.9, 126.5, 126.7, 129.8, 132.5, 133.3, 135.2, 135.4, 141.7, 143.2, 153.3, 153.7. IR (KBr pellet, cm^{-1}): 3642 (ν_{O-H}). MS (*m*/*z*): 564, 566 (M$^+$, M$^+$ + 2), calcd for M = 565.6.

1-Bromo-2,4-bis(3,5-di-*tert*-butyl-4-acetoxyphenyl)benzene (9). **9** was prepared in the same manner of **7** using **8** to give white crystals: yield 75%; mp 231−232 °C. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm): δ 1.40 (s, 36H, *tert*-butyl), 2.38 (s, 6H, −CH$_3$), 7.35−7.71 (m, 7H, phenyl). ^{13}C NMR (CDCl$_3$, ppm): 22.7, 31.5, 35.6, 121.6, 125.4, 127.5, 127.9, 130.3, 133.4, 137.1, 137.6, 141.4, 141.8, 142.7, 142.9, 147.4, 147.8, 172.4. IR (KBr pellet, cm^{-1}): 1762 ($\nu_{C=O}$). MS (*m*/*z*): 648, 650 (M$^+$, M$^+$ + 2), calcd for M = 649.7.

2-Bromo-3,5-Bis(3,5-di-*tert*-butyl-4-aceotoxyphenyl)styrene (3). *N*-Bromosuccinimide (0.37 mg, 2.1 mmol) and α,α′-azobis(isobutyronitrile) (a few mg) were suspended in the CCl$_4$ solution (3.8 mL) of 2-bromo-3,5-bis(3,5-di-*tert*-butyl-4-aceotoxyphenyl)toluene (1.2 g, 2.1 mmol) and refluxed until succinimide floated on the solution. The mixture was cooled to room temperature and filtered off. After the filtrate was evaporated, benzene (4.1 mL) and triphenylphosphine (0.54 g, 2.1 mmol) were added to it. The resulting solution was stirred at 50 °C for 18 h. The solution was poured into diethyl ether to give the phosphonium salt (1.4 g): yield 73%. The phosphonium salt (1.4 g) was suspended in 25% formaldehyde (20 mL) and H$_2$O (10 mL), and 5 N NaOH (5 mL) was added dropwise over 20 min at room temperature. The mixture was stirred for 1.5 h and extracted with ether. The extract was washed with water, dried over anhydrous sodium sulfate, and then evaporated. The crude product was purified by silica gel column separation with a hexane/CHCl$_3$ (1/2) eluent to give a pale yellow powder. It was recrystallized from hexane to give white crystals: yield 84%; mp 227−228 °C. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm): δ 1.40 (s, 36H, *tert*-butyl), 2.38 (s, 6H, −O−CO−CH$_3$), 5.43 (d, 1H, 11 Hz, −CH═C**H**$_2$), 5.76 (d, 1H, 17 Hz, −CH═C**H**$_2$), 7.23 (dd, 1H, 11 Hz, 17 Hz, −C**H**═CH$_2$), 7.52 (s, 2H, phenyl), 7.40 (s, 2H, phenyl), 7.45 (d, 2H, 2.4 Hz, phenyl), 7.52 (s, 2H, phenyl), 7.64 (d, 1H, 2.3 Hz, phenyl). ^{13}C NMR (CDCl$_3$, ppm): δ 22.7, 22.8, 31.5, 35.6, 117.2, 122.9, 124.9, 125.5, 128.0, 129.6, 137.2, 137.3, 138.2, 139.0, 140.8, 141.8, 142.9, 143.7, 147.3, 147.9, 171.1, 171.2. IR (KBr pellet, cm^{-1}): 1763 ($\nu_{C=O}$), 1626 ($\nu_{C=C}$). MS (*m*/*z*): 674, 676 (M$^+$, M$^+$ + 2), calcd for M = 675.3.

Polymerization. Palladium acetate (33.2 mg, 0.15 mmol), tri-*o*-tolylphosphine (90.0 mg, 0.3 mmol), and triethylamine (1.45 g, 14.3 mmol) were added to a DMF solution (2.0 mL) of **3** (80 mg, 32.0 μmol). The solution was heated at 90 °C for 24 h under nitrogen. The mixture was separated using a polystyrene gel column with a CHCl$_3$ elution and was purified by reprecipitation from CHCl$_3$ in methanol to yield the polymer as a yellow powder (**1b**): yield 63%. ^{1}H NMR (CDCl$_3$, 500 MHz; ppm): δ 1.34 (s, 36H, *tert*-butyl), 2.37 (s, 6H, −O−CO−CH$_3$), 7.25−7.50 (m, 6H, Ar, −HC═CH−). IR (KBr pellet, cm^{-1}): 1764 ($\nu_{c=o}$), 967 ($\delta_{\mathrm{trans HC=CH}}$). The molecular weight of the polymer was measured by a light-scattering molecular weight analyzer (Tosoh LS-8000). Bromide content = 1.6%, as determined by the combustion method.

1b (210 mg) was dissolved in a slight amount of THF. To its suspension in DMSO (32 mL) was added 2.5 N KOH (7 mL); the solution was stirred at 40−50 °C for 12 h, cooled to room temperature, and neutralized with 1 N HCl. The organic product was extracted with CHCl$_3$, washed with water, and dried over anhydrous sodium sulfate. The CHCl$_3$ layer was evaporated and poured in methanol to yield **1c**: yield 86%. ^{1}H NMR (CDCl$_3$, 500 MHz; ppm): δ 1.39 (s, 36H, *tert*-butyl), 5.24 (s, 6H, OH), 7.04−7.43 (m, 6H, Ar, −HC═CH−). IR (KBr pellet, cm^{-1}): 3638 (ν_{O-H}), 952 ($\delta_{\mathrm{trans HC=CH}}$).

2,4,3′,5′-Tetrakis(3,5-di-*tert*-butyl-4-acetoxyphenyl)stilbene (2b). Palladium acetate (22.6 mg, 0.101 mmol), tri-*o*-tolylphosphine (61.2 mg, 0.202 mmol), and triethylamine (2.5 g, 24.8 mmol) were added to a DMF (4.0 mL) solution of 3,5-bis(3,5-di-*tert*-butyl-4-aceotoxyphenyl)styrene (0.30 g, 0.05 mmol) and 1-bromo-2,4-bis(3,5-di-*tert*-butyl-4-acetoxyphenyl)benzene (0.33 g, 0.05 mmol). The solution was warmed to 95 °C for 24 h, cooled to room temperature, and extracted with CHCl$_3$. The organic layer was evaporated, and the crude product was purified by silica gel column separation with a hexane/CHCl$_3$ (1/2) eluent to give a pale yellow solid of **2b**: yield 65%. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm): δ 1.40 (s, 72H, *tert*-butyl), 2.38 (s, 12H, −O−CO−CH$_3$), 6.71−7.86 (m, 16H, Ar, −HC═CH−). ^{13}C NMR (CDCl$_3$, ppm): δ 21.2, 31.5, 35.6, 124.3, 125.5, 125.6, 126.3, 126.4, 126.6, 128.4, 128.6, 130.0, 130.1, 133.0, 134.4, 137.4, 138.3, 138.4, 141.6, 142.0, 142.6, 142.7, 142.8, 143.4, 147.6, 171.1. IR (KBr pellet, cm^{-1}): 1763 ($\nu_{C=O}$), 965 ($\delta_{\mathrm{trans HC=CH}}$). FAB-MS (*m*/*z*): 1165 (found), calcd for M = 1165.6.

2,4,3′,5′-Tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)stilbene (2c). **2b** (210 mg) was dissolved in a slight amount of THF. To its suspension in DMSO (32 mL) was added 2.5 N KOH (7.0 mL); the solution was stirred at 40−50 °C for 12 h, cooled to room temperature, and neutralized with 1 N HCl. The organic product was extracted with CHCl$_3$, washed with water, and dried over anhydrous sodium sulfate. The CHCl$_3$ layer was evaporated, and the crude product was purified by silica gel column separation with a hexane/CHCl$_3$ (2/1) eluent to give a pale yellow solid of **2c**: yield 86%. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm): δ 1.40 (s, 72H, *tert*-butyl), 5.26 (s, 4H, −OH), 6.98−7.86 (m, 16H, Ar, −HC═CH−). ^{13}C NMR (CDCl$_3$, ppm): δ 30.5, 34.5, 122.8, 123.5, 124.1, 124.3, 125.3, 125.7, 126.3, 126.9, 128.5, 128.7, 128.8, 132.3, 132.8, 133.0, 135.4, 136.2, 136.3, 138.4, 141.4, 142.4, 143.1, 153.1, 153.5, 153.6. IR (KBr pellet, cm^{-1}): 3640 (ν_{O-H}), 967 ($\delta_{\mathrm{trans HC=CH}}$). FAB-MS: (*m*/*z*) 997 (found), calcd for M = 997.5.

2,4-Bis(3,5-di-*tert*-butyl-4-acetoxyphenyl)stilbene (12b) and 3,5-Bis(3,5-di-*tert*-butyl-4-acetoxyphenyl)stilbene (13b). **12b** and **13b** were prepared in the same manner of **1b** using **9** and styrene, and **11b** and bromobenzene, respectively.

Palladium acetate, tri-*o*-tolylphosphine, and triethylamine were added to a DMF solution of **9** and styrene or **11b** and bromobenzene. The solution was warmed to 90 °C for 12 h, cooled to room temperature, and extracted with $CHCl_3$. The organic layer was evaporated, and the crude product was purified by silica gel column separation with a hexane/$CHCl_3$ (1/2) eluent to give a pale yellow solid of **12b**: yield 67%. ^1H NMR ($CDCl_3$, 500 MHz, ppm): δ 1.37 (s, 36H, *tert*-butyl), 2.36 (s, 6H, $-O-CO-CH_3$), 6.75−7.78 (m, 14H, Ar, $-HC{=}CH-$). ^{13}C NMR ($CDCl_3$, ppm): δ 21.5, 31.3, 35.6, 121.8, 123.8, 123.9, 125.7, 126.1, 126.2, 127.5, 127.9, 128.2, 132.5, 132.8, 134.8, 135.0, 136.1, 140.1, 147.3, 170.8. IR (KBr pellet, cm^{-1}): 1765 ($\nu_{C=O}$), 962 ($\delta_{transHC=CH}$). FAB-MS (*m*/*z*): 673 (found), calcd for M = 672.9. **13b**: yield 73%. ^1H NMR ($CDCl_3$, 500 MHz, ppm): δ 1.34 (s, 36H, *tert*-butyl), 2.32 (s, 6H, $-O-CO-CH_3$), 6.81−7.70 (m, 14H, Ar, $-HC{=}CH-$). ^{13}C NMR ($CDCl_3$, ppm): δ 21.5, 31.3, 35.6, 121.3, 124.0, 124.7, 124.8, 125.7, 126.2, 127.6, 128.0, 132.6, 134.8, 136.0, 136.7, 141.5, 152.3. IR (KBr pellet, cm^{-1}): 1765 ($\nu_{C=O}$), 963 ($\delta_{transHC=CH}$). FAB-MS (*m*/*z*): 673 (found), calcd for M = 672.9.

12c and **13c** were prepared in the same manner of **11c**. **12c**: yield 83%. ^1H NMR ($CDCl_3$, 500 MHz, ppm): δ 1.38 (s, 36H, *tert*-butyl), 5.28 (s, 2H, $-OH$), 6.95−7.81 (m, 14H, Ar, $-HC{=}CH-$). ^{13}C NMR ($CDCl_3$, ppm): δ 30.5, 34.5, 122.2, 124.5, 124.7, 125.8, 126.0, 126.1, 127.2, 127.5, 128.2, 128.4, 132.7, 134.5, 134.9, 136.3, 152.8. IR (KBr pellet, cm^{-1}): 3645 (ν_{O-H}), 963 ($\delta_{transHC=CH}$). FAB-MS: (*m*/*z*) 589 (found), calcd for *M* = 588.9. **13c**: yield 77%. ^1H NMR ($CDCl_3$, 500 MHz, ppm): δ 1.36 (s, 36H, *tert*-butyl), 5.30 (s, 2H, $-OH$), 6.75−7.63 (m, 14H, Ar, $-HC{=}CH-$). ^{13}C NMR ($CDCl_3$, ppm): δ 21.3, 35.2, 121.7, 123.5, 124.1, 124.2, 126.4, 126.9, 127.5, 1287.3, 133.8, 135.2, 136.5, 137.4, 144.8, 153.0. IR (KBr pellet, cm^{-1}): 3638 (ν_{O-H}), 962 ($\delta_{transHC=CH}$). FAB-MS: (*m*/*z*) 589 (found), calcd for M = 588.9.

Preparation of the Poly- and Tetraradicals. An aqueous sodium hydroxide (1 mL, 20 equiv to the phenol) was added to a toluene solution (2 mL) of the phenol precursor (20 unit mM), and the solution was stirred for 0.5 h under a nitrogen atmosphere in a glovebox. The solution was then vigorously stirred with 1 mL of aqueous potassium ferricyanide (20 equiv to the phenolate) at room temperature. The organic layer turned from green to purple and finally to orange-brownish in response to the radical concentration formed. After the mixture was stirred for 0.5 h, the organic layer was washed with water and dried over anhydrous sodium sulfate to give the radical solution.

The poly- and tetraradicals were also prepared by the heterogeneous oxidation with lead oxide. A toluene solution of the phenol precursor (20 unit mM) was treated with 10 equiv freshly prepared lead oxide. The radical derivatives were given after filtration.

ESR. ESR spectra were taken using a JEOL JES-TE200 ESR spectrometer with 100 kHz field modulation. The spin concentration of each sample was determined based on the assumption of $S = {}^1/_2$ at room temperature by integration of the ESR signal standardized with that of a TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxyl) solution. The spin concentration was also analyzed with the slope of Curie plots and the saturated magnetization in the SQUID measurement. These spin concentration values were almost consisted with each other.

Electrochemical Measurements. A voltammetric investigation was carried out in CH_2Cl_2 in the presence of 0.1 M $(n\text{-}C_4H_9)_4NBF_4$ as a supporting electrolyte and a small amount of $(n\text{-}C_4H_9)_4NOH$ as an alkaline with a platinum working electrode using a function generator (Nikko Keisoku NPG-3) and a potentiogalvanostat (NPGS-301) at a scan rate 50 mV. For coulometry, a glassy carbon disk-platinum ring was used as a working electrode and the reference electrode was a commercial Ag/AgCl. Coulometric electrolysis was performed using a digital coulomb meter (Nikko Keisoku NDCM-1). All the electrochemical experiments were carried out in the absence of oxygen.

Magnetic Measurement. The toluene solution of the phenoxyl radical was immediately transferred to a diamagnetic capsule after the oxidation. 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, and 5 K. The static magnetic susceptibility was measured from 2 to 200 K at a field of 0.5 T. Ferromagnetic magnetization ascribed to impurities (<20 ppm) was determined by Honda−Owen plots and subtracted from the overall magnetization. Diamagnetic susceptibility (χ_{dia}) of the sample solution and the capsule was estimated by the Curie plots of magnetic susceptibility.

Other Spectroscopic Measurements. The ^1H and ^{13}C NMR, MS, FAB-MASS, UV/vis, IR, and fluorescence spectra were measured using a JEOL Lambda 500, a Shimadzu GCMS-QP5050, a JMS-SX-102A, a JASCO V-500, a JASCO FT/IR-410, and a Hitachi F-4500 spectrometer, respectively.

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(12) Torsional angles between the 3,5-bearing pendant groups and the main poly(1,2-phenylenevinylene) chain was estimated to be 36−40° in the CVFF force field calculation for **1b**.

(13) Q was estimated from the equation of $Q = nCFV$, where n, C, F, and V are the electron-transfer number per phenol unit, the concentration of the phenol unit, Faraday's constant (9.6486×10^4 C/equiv), and the solution volume.

(14) $\chi_{\mathrm{mol}}T = (N_{\mathrm{A}}g^2\mu_{\mathrm{B}}{}^2T)/(k(T - \theta))[x_3\{1 + \exp(-2J/kT) + 10\exp(J/kT)\}/12\{1 + \exp(-2J/kT) + 2\exp(J/kT)\} + x_2/(3 + \exp(-2J/kT)) + x_1/4]$, where x_1, x_2, and x_3 are the fractions of the doublet, the triplet, and the quartet, respectively ($x_1 + x_2 + x_3 = 1$). μ_{B} and θ are the Bohr magneton and the Weiss constant, respectively: Vleck, J. H. V. *The Theory of Electric and Magnetic Susceptibilities*; Oxford University Press: London, 1932.

(15) A four-spin model with at least two different J values would be appropriate for a system with four radical sites. However, the average S value was determined to be 2/2 for **2a** by the magnetic measurement. Thus we applied the equation for a three-spin system to approximate J for a coupling between the neighboring sites: Kaneko, T.; Toriu, S.; Nii, T.; Tsuchida, E.; Nishide, H. *Mol. Cryst. Liq. Cryst.* **1995**, *272*, 153.

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