

High-Spin Polyphenoxyls Attached to Star-Shaped Poly(phenylenevinylene)s

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Star-shaped poly(1,2-phenylenevinylene)s 4-substituted with multiple pendant phenoxy (2 and 3) were synthesized by polymerizing 2-bromo-4-(acetoxypheyl)styrene in the presence of 1,3,5-triiodobenzene or 1,3,5-tris(3',5'-diiodophenyl)benzene as the core via a simple one-pot Heck reaction and subsequent hydrolysis, phenolate formation, and heterogeneous oxidation. ESR spectra indicated a delocalized spin distribution into the core parts of the star-shaped molecules. The polyradicals, 2 and 3, were in a high-spin state at low temperature, and the ferromagnetic behavior was enhanced for the polyradical with a higher molecular weight. Although an average S of 3 remained at 3/2 to 4/2, the polyradical 2 even with a spin concentration of 0.8 spin/unit revealed an average S of 7/2 to 8/2. The 1,3,5-benzene core acted as an effective magnetic coupler to align the spins of the pendant phenoxy through the star-shaped π -conjugated backbone.

Introduction

The research on very high-spin organic molecules using intramolecular through-bond magnetic ordering has been exhaustively continued in connection with realizing purely organic-derived and unknown magnetism.^{1,2} Among these efforts, there is an approach to design and synthesize a π -conjugated linear polymer bearing multiple pendant radical groups, which are attached to one π -conjugated backbone that satisfies a ferromagnetic connectivity of the radicals.³ In this type of polyradical, a radical or spin defect, which is unavoidable for radical polymers with an increase in molecular size, is not fatal to the spin alignment between the pendant unpaired electrons, because the spin-coupling interaction occurs through the π -conjugated polymer backbone. Additionally, multiple numbers of spin are accumulated along one backbone, and the spins are expected to interact among not only their neighboring spins but also their remote spins through the π -conjugated backbone. Besides these advantages, a chemically stable organic radical species can be introduced on a polyradical as the pendant group. The resultant polyradical has substantial stability and is easily handled, e.g., at room temperature. We recently synthesized poly(1,2-phenylenevinylene) bearing di-*tert*-butylphenoxy as the pendant radical group (1) because of the coplanarity in the π -conjugated linear backbone and of the delocalized spin density distribution of the radical moiety, and we have for the first time reported a through-conjugated backbone bond and long-range fer-

romagnetic spin-coupling interaction between the pendant unpaired electrons.⁴ The polyradical 1 with a spin concentration of 0.7 spin/monomer unit or /phenoxy precursor group displayed a spin quantum number (S) at low temperature of 4/2 to 5/2.

Prior to and parallel with the approach using pendant-type polyradicals, high-spin alignment at low temperature has been demonstrated for cross-conjugated polyradicals such as poly(1,3-phenylenecarbene)^{1b} and poly(1,3-phenylenephnylmethine).^{1c} They have been recently extended to their (pseudo-)two-dimensional homologues, i.e. branched, dendric, macrocyclic, annelated macrocyclic, and pseudo-ladder polyradicals.^{2,5} Such two-dimensional extensions successfully brought about the increase in S ; the extensions, especially the macrocyclic ones, diminished the damage of a spin defect by guaranteeing plural pathways of the spin-coupling interaction in the two-dimensional frameworks. A spin defect is fatal for the cross-conjugated polyradicals because their radicals are formed in the backbone through cross-conjugated structures and a spin defect breaks down their π -conjugation. In addition to this problem, these carbon-centered polyradicals are far too unstable to make a practicable material. To improve such a two-dimensional strategy for organic polyradicals with high spin alignment, we extended in this paper⁶ our pendant-type polyradical 1, which is characterized by chemical stability and spin-defect-insensitivity, to the star-shaped homologues, 2 and 3, star-shaped poly(1,2-phenylenevinylene)s bearing 4-substituted pendant phenoxy radicals.

Results and Discussion

Synthesis and Characterization of the Precursor Star-Shaped Polyphenols. A restricted primary struc-

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ture or complete head-to-tail linkage of the monomer unit is essential for a ferromagnetic spin alignment in the pendant-type polyradical, which was established in this study through the polymerization via the Heck reaction,⁷ or the arylation of an olefin with an aryl bromide catalyzed by a palladium–phosphine complex, of a bromostyrene derivative, 2-bromo-4-(3',5'-di-*tert*-butyl-4'-acetoxyphenyl)styrene (**4**).⁴ The acetoxy polymer **6** was synthesized through a one-pot reaction of **4** via the Heck reaction using a catalyst of palladium acetate and tri-*o*-tolylphosphine, in the presence of 1,3,5-triiodobenzene (**5**) as the core of the star-shaped polymer. **5** was selected as the core because of its higher reactivity in the Heck reaction than **4**. In addition, a strong ferromagnetic coupling effect of the 1,3,5-benzene ring has been reported for 1,3,5-tris(di-*p*-biphenylmethyl)benzene,^{8a} 1,3,5-tris(3',5'-*tert*-butyl-4'-oxyphenyl)benzene,^{8b} and 1,3,5-benzenetriyltris(*N*-*tert*-butylnitroxide).^{8c} The iodide of **5** was initially and completely reacted with **4** at 45 °C, and heating to 90 °C allowed the reaction of the bromide of **4** to yield the phenylenevinylene polymer. The molecular weight or degree of polymerization (DP, = $l + m + n$ in **2**) of the star-shaped polymer was controlled by the feed ratio of **4/5** in the polymerization.

The **6** polymers were obtained as yellow powders that were soluble in common solvents such as benzene, THF, and CHCl₃. The iodo site of the core **5** was completely reacted in every polymer, which was confirmed by the iodine content of less than 0.01% determined by the combustion method and X-ray fluorometry. Fourteen aromatic carbon absorption peaks in ¹³C NMR ascribed to the benzene rings and vinylene supported both the head-to-tail linkage structure of the branch chains and vinylene-substituted benzene structure of the core (for details, see Experimental Section). The *trans*-stilbene structure was supported by fluorescence at 450 nm ($\lambda_{\text{ex}} = 420$ nm) and IR absorption attributed to an out-of-plane bending mode of the *trans*-vinylene at 960 cm⁻¹. The precursor acetoxy polymer **6** was converted to the corresponding hydroxy polymer **7** after complete elimination of the protecting acetyl group in alkaline solution. DP was measured by a light-scattering molecular weight analysis; e.g., **7** with DP = 70 determined by the light-scattering analysis and DP = 68 by bromide analysis (for details, see Experimental Section). The agreement in the DP values supports a linear structure of the branch chains. Three hydroxy polymers **7** with different DP or molecular weight were synthesized (Table 1).

The hydroxy polymer **7** was converted to a deeply red-colored phenolate anion of the polymer (**8**) with a small excess of tetra(*n*-butyl)ammonium hydroxide in THF. Quantitative formation of the phenolate anion **8** was detected by a complete disappearance of 6.2 ppm ascribed to the phenolic proton in NMR of the THF-*d*₆ solution of **7** under the constant integration values of aromatic and *tert*-butyl protons, after alkaline addition to the **7** THF solution. **8** was heterogeneously oxidized with an aqueous K₃FeCN₆ phase to yield the polyradical **2**. **2** was also soluble in common solvents. **2** was isolated as a brownish

Table 1. Molecular Weight of the Hydroxy Polymers and Average Spin Quantum Number of the Polyradicals

| hydroxy polymer | yield (%) ^a | mol wt ^b (DP) ^c | M_w/M_n ^d | polyradical | spin concn (spin/unit) | S^e |
|-----------------|------------------------|---------------------------------------|------------------------|-------------|------------------------|------------|
| 7 | 42 | 2.1×10^4 (70) | 1.2 | 2 | 0.80 | 7/2 to 8/2 |
| 7 | 45 | 1.3×10^4 (42) | 1.2 | 2 | 0.70 | 6/2 to 7/2 |
| 7 | 48 | 1.0×10^4 (33) | 1.2 | 2 | 0.72 | 5/2 to 6/2 |
| 12' | | 1913 (6) | | 12 | 0.83 | 4/2 to 5/2 |
| 11' | | 996 (3) | | 11 | 0.91 | 3/2 |
| 1' | 40 | 5.7×10^3 (17) | 1.2 | 1 | 0.68 | 4/2 to 5/2 |
| 15 | 62 | 1.1×10^4 (34) | 1.2 | 3 | 0.63 | 3/2 to 4/2 |
| 18' | | 2142 (6) | | 18 | 0.88 | 2/2 |

^a Yield for the polymerization of the precursor acetoxy polymer. ^b Average molecular weight measured by the light-scattering method for **7**, **1'**, and **15**, and molecular weight measured by mass spectroscopy for **12'**, **11'**, and **18'**. ^c Average degree of polymerization for **7**, **1'**, and **15**, and number of hydroxyphenylstyrene units represented in Schemes 2 and 4 for **12'**, **11'**, and **18'**, respectively. ^d Ratio of the number- and weight-average molecular weight measured by gel-permeation chromatography. ^e Average spin quantum number for the spin state at 2–5 K.

green powder which was chemically stable at room temperature even in air. For example, the half-life of the radical in **2** was 3.4 days at room temperature.

As core-combined tri- and hexaradical compounds, their precursors, 1,3,5-tris[4'-(3'',5''-di-*tert*-butyl-4'-acetoxyphenyl)styryl]benzene (**11'**) and 1,3,5-tris[2'-styryl-{4',5''-bis(3,5-di-*tert*-butyl-4-acetoxyphenyl)stilbene}]benzene (**12'**), were also synthesized via the same palladium-catalyzed Heck reaction.

The polyradicals having six π -conjugated branch chains **3** were also synthesized from the core of 1,3,5-tris(3',5'-diiodophenyl)benzene (**13**). **13** was prepared via benzene ring formation of 3,5-diiodoacetophenone. In the presence of **13**, **4** was polymerized using the palladium–phosphine catalyst at 45 °C and then 90 °C in a similar manner for the **6** synthesis already described. The six iodo sites of **13** were completely reacted with **4**. The acetoxy polymer **14** was a yellow powder, soluble in common solvents, and was characterized, in the same manner for **6** (for details, see Experimental Section). **14** was completely hydrolyzed to the hydroxy polymer **15** (Table 1). **15** was converted to the corresponding phenolate polymer **16** through alkaline treatment and was then heterogeneously oxidized to yield the polyradical **3**. The brownish green **3** was also soluble in common solvents such as benzene, THF, and CHCl₃. The half-life of the radical was 1.4 days for **3** in powder state at room temperature.

The 1,3,5-triphenylbenzene-combined hexaradical compound **18** was also synthesized by the same Heck reaction of **9** with 1,3,5-tris(3',5'-dibromophenyl)benzene.

ESR Spectra of the Polyradicals. The ESR spectra of **2** and **3** at a low spin concentration (spin concn) gave a broad hyperfine structure at $g = 2.004_2$ attributed to the 5–7 protons of the phenoxyl ring and phenylenevinylene backbone, which was in contrast to the three-line hyperfine structure of 2,4,6-tri-*tert*-butylphenoxyl or that attributed to an unpaired electron localized in the phenoxyl ring. The proton hyperfine structures were more clearly observed for the core-combined triradical and hexaradical models, **11** and **18**, at a low spin concn (Figure 1a,b, respectively). The dashed line of Figure 1a shows a simulation of the hyperfine structure for **11**, which gave the a_{H} values of 0.09 mT attributed to the vinylene protons and those of 0.08 mT attributed to the protons of the 1,3,5-trisubstituted benzene core. These ESR results suggest an effectively delocalized spin dis-

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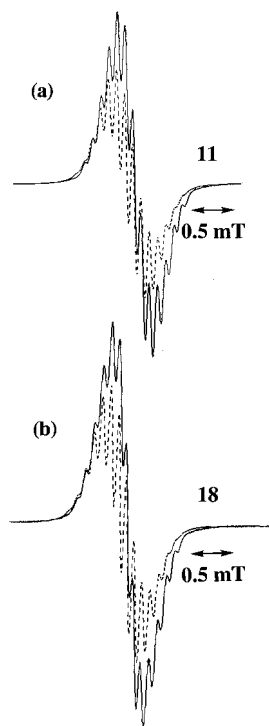


Figure 1. ESR spectra of the tri- and hexaradicals at room temperature. Phenoxy precursor concn = 0.5 unit mM. (a) Triradical **11** with spin concn = 0.08 in toluene at $g = 2.0042$; the dashed line for the simulation with $a_H = 0.10, 0.09$, and 0.08 mT. (b) Hexaradical **18** with spin concn = 0.12 in toluene at $g = 2.0042$; a_H for the simulation with $0.10, 0.09$, and 0.08 mT.

tribution over the entire star-shaped polyradical **2** probably because of its less hindered steric structure. The hyperfine structure for **18** (Figure 1b) resembles that for **11**; a simulation gave the a_H values of 0.09 mT attributed to the vinylene protons and those of 0.08 mT attributed to the protons of the outer 1,3,5-benzene ring substituted with two branch phenoxy groups and one core benzene. However, any further splitting to be ascribed to the protons of the core benzene was not observed. These results suggest for the hexaradical model **11** a spin density distribution into the outer three benzene rings from the branch polyphenoxyl chains but not into the core benzene or the inner part of the core.

The ESR spectra of **2** and **3** showed sharp and unimodal signals with increasing spin concn, indicating a locally high spin concn along the polymer backbones. A frozen toluene glass of **2** with a spin concn of 0.7 spin/unit gave a $\Delta M_s = \pm 2$ forbidden transition ascribed to a triplet species at $g = 4$ (inset in Figure 2). The ESR signal in the $\Delta M_s = \pm 2$ region was doubly integrated to give Curie plots (Figure 2). Although the signal intensity is proportional to the reciprocal of the temperature ($1/T$) at higher temperature, the plots deviate upward from linearity in the lower temperature (< 35 K) region. This upward deviation supports a multiplet ground state for the polyradical **2**.

Magnetic Properties. Magnetization and static magnetic susceptibility of the polyradicals **2**, **11**, and **12**, in frozen 2Me-THF or toluene, were measured using a SQUID magnetometer. The magnetization (M) normalized with saturated magnetization (M_s) for **2** with DP = 70 and spin concn = 0.80 is plotted vs the effective temperature ($T - \theta$) (Figure 3), where θ is a coefficient

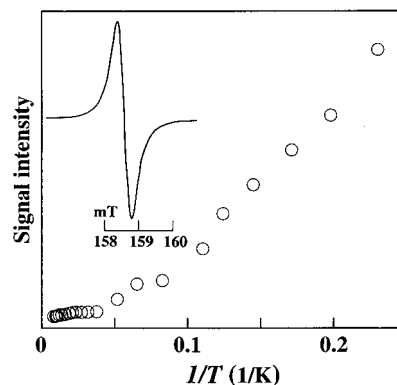


Figure 2. Curie plots for the peak in the $\Delta M_s = \pm 2$ region for the polyradical **2** with spin concn = 0.70 spin/unit in toluene glass. Phenoxy precursor concn = 30 unit mM. Inset: $\Delta M_s = \pm 2$ spectrum.

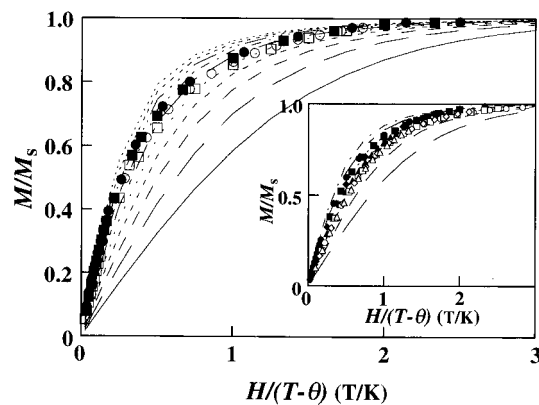


Figure 3. Normalized plots of magnetization (M/M_s) vs the ratio of magnetic field and temperature ($H/(T - \theta)$) for the polyradical **2** with DP = 70 and a spin concn = 0.80 spin/unit in frozen 2Me-THF at $T = 1.8$ (●), 2.0 (■), 2.5 (○), and 3 (□) K, and the theoretical curves corresponding to the $S = 1/2, 2/2, 3/2, 4/2, 5/2, 6/2, 7/2, 8/2, 9/2$, and $10/2$ Brillouin functions. Inset: M/M_s vs $H/(T - \theta)$ plots (closed) for the hexaradical **12** with spin concn = 0.83 spin/unit at $T = 2.0$ (●), 2.5 (■), 3.0 (◆), and 5.0 (▲) K; the plots (open) for the triradical **11** with spin concn = 0.91 spin/unit at $T = 2.0$ (○), 2.5 (□), 3.0 (◇), and 5.0 (△) K; and the theoretical curves corresponding to the $S = 1/2, 2/2, 3/2, 4/2, 5/2$, and $6/2$ Brillouin functions.

of a weak antiferromagnetic interaction between radicals and is determined from curve fitting using the following $\chi_{\text{mol}} T$ vs T data. The M/M_s plots are compared with the theoretical Brillouin curves for $S = 1/2$ to $10/2$. It should be noted here that, for a disperse spin system, an "average" Brillouin function is never followed in a strict manner for monodisperse spin systems and that the M/M_s tends to decrease at high fields due to lower S fragments such as $S = 1/2, 2/2$, and $3/2$, as has been previously discussed.^{5a} The M/M_s plots of the polyradical **2** are close to the Brillouin curves for $S = 9/2$ at low fields and lie almost on the curve for $S = 6/2$ at high fields. This indicates a ferromagnetic coupling, on the average, between seven or eight unpaired electrons at low temperature. The magnetization plots for **2** with DP = 42 and 33 were also measured and compared with the Brillouin curves to give the average S values in Table 1.

The inset in Figure 2 shows the M/M_s plots for **12** with a spin concn = 0.83 and **11** with a spin concn = 0.91 , which indicate that $S = 4/2$ to $5/2$ and $3/2$ at low temperature for **12** and **11**, respectively. The latter

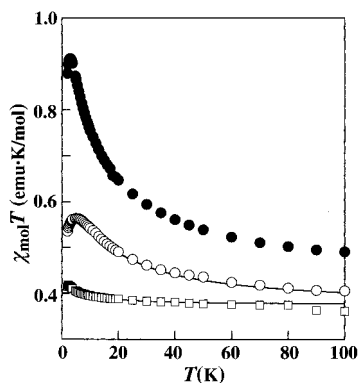


Figure 4. $\chi_{\text{mol}}T$ vs T plots (●) of the polyradical **2** with DP = 70 and spin concn = 0.80 spin/unit, (○) of the triradical **11** with spin concn = 0.91 spin/unit, and (□) of the biradical **19** with spin concn 0.72 spin/unit in frozen 2Me-THF. Solid lines are theoretical curves calculated using eq 1 for **11** ($2J = 19 \text{ cm}^{-1}$, $\theta = -0.29 \text{ K}$, $x_1 = 0$, $x_2 = 0.13$, $x_3 = 0.87$) and using the Bleaney–Bowers expression for **19** ($2J = 6 \text{ cm}^{-1}$, $x_1 = 0.34$, $x_2 = 0.66$).

indicates a quartet ground state of the triradical **11**. These results mean that the 1,3,5-substituted benzene acts as an effective coupler to connect three branch polyradical chains.

Figure 4 shows the product of molar magnetic susceptibility (χ_{mol}) and T vs T for the polyradicals **2** (DP = 70, spin concn = 0.80). $\chi_{\text{mol}}T$ is much larger than the theoretical value ($\chi_{\text{mol}}T = 0.375$) for $S = 1/2$ and increases at low temperature, which indicates a strong ferromagnetic behavior. The $\chi_{\text{mol}}T$ increase at low temperature was decreased for the polyradical **2** with a lower molecular weight. The figure also gives the $\chi_{\text{mol}}T$ plots for the core-combined triradical **11** and the biradical analogue of **1** or of the branch polyphenoxy chain (**19** in Chart 2). They exhibit not a strong but a ferromagnetic $\chi_{\text{mol}}T$ increase.

The M/M_s plots of **19** were presented close to the Brillouin curve for $S = 2/2$ at low temperature, indicating a triplet ground state of the biradical **19**. $\chi_{\text{mol}}T$ vs T plots of **19** in Figure 4 were analyzed using the Bleaney–Bowers expression⁹ to estimate the spin-exchange coupling constant (J) in the biradical. Curve fitting of the $\chi_{\text{mol}}T$ data for **19** in Figure 4 (the solid line) yielded the exchange coupling constant or a triplet–singlet energy gap $2J = 6 \pm 1 \text{ cm}^{-1}$ (other parameters given in the caption of Figure 4). The triradical **11** with $S \leq 3/2$ could be expressed as the mixture of a three-, two-, and one-spin system, and its $\chi_{\text{mol}}T$ could be analyzed, as a first approximation, using the following van Vleck expression:¹⁰

$$\chi_{\text{mol}}T = \frac{N_A g^2 \mu_B^2 T}{k(T - \theta)} \left[\frac{x_3}{12} \frac{1 + \exp(-2J/kT) + 10 \exp(J/kT)}{1 + \exp(-2J/kT) + 2 \exp(J/kT)} + \frac{x_2}{3 + \exp(-2J/kT)} + \frac{x_1}{4} \right] \quad (1)$$

where x_1 , x_2 , and x_3 are the fraction of the doublet, the

triplet, and the quartet, respectively ($x_1 + x_2 + x_3 = 1$). The $\chi_{\text{mol}}T$ data of **11** in Figure 4 were analyzed (the solid line in Figure 4 is curve-fitted to eq 1) to give $2J = 19 \pm 2 \text{ cm}^{-1}$ for **11**. This exchange coupling constant is larger than that for the biradical analogue of the branch polyphenoxy chain (**19**), which also involves the conjugated but spacing phenylenevinylene unit. This result supports the fact that the 1,3,5-benzene core acts as an effective coupler to connect three branch polyradical chains.

The M/M_s plots of the hexaradical **18** with spin concn = 0.88 lay almost on the Brillouin curve for $S = 2/2$; the hexaradical **18** remained at a triplet ground state. The $\chi_{\text{mol}}T$ vs T plots of **18** are given in the inset in Figure 5 and were analyzed using eq 1 (the solid line for curve fitting) to yield $2J = 19 \pm 3 \text{ cm}^{-1}$. This $2J$ value agrees with that for the triradical **11** and supports the spin-coupling interaction of two phenoxy groups through the same conjugated spacer of phenylenevinylene–*m*-phenylene–vinylene–phenylene for both **18** and **11** (see Schemes 2 and 4). However, **18** did not display any effect of the inner core of the 1,3,5-benzene coupler on the S and $2J$ value or the ferromagnetic coupling interaction.

The inset of Figure 5 also shows the $\chi_{\text{mol}}T$ data for the hexabranched polyradical **3** with DP = 34 and spin concn = 0.63. $\chi_{\text{mol}}T$ and its increase at low temperature were larger than those of the hexaradical **18**. However, the M/M_s plots of the polyradical **3** remained almost on the Brillouin curve of $S = 3/2$ (Figure 5). The hexabranched extension based on the core of 1,3,5-tris(3',5'-disubstituted phenyl)benzene failed in increasing the S value or the spin-coupling interaction between the phenoxy groups attached to the star-shaped π -conjugated backbone.

In the polyradical **3**, the inner core benzene could not magnetically couple the outer-phenyl-substituted six polyphenoxy branch chains, despite the totally π -conjugated primary structure of **3**. Two reasons are considered for this insufficient connectivity between the three outer-phenyl rings and the inner or central 1,3,5-benzene ring. (i) Biphenyl is not a strong magnetic coupler because of the twisted and noncoplanar biphenyl linkage. In addition, the 3'-outer-phenyl-substituted branch chains sterically hinder the branch chains 5'-substituted on the neighboring outer phenyls for **3** and **18**. (ii) Borden and Davidson proposed a concept of disjoint and nondisjoint connectivity of nonbonding molecular orbitals (NBMOs) to estimate the stability of a triplet ground state of a biradical molecule.¹¹ By applying this concept to the core of **3** and **18**, 1,3,5-tris(3',5'-diradical-substituted phenyl)benzene (Chart 3), the NBMOs cannot be localized in disjoint groups (i.e., nondisjoint), and a triplet ground state is stabilized with sufficient $2J$ for the biradical part connected with the phenylenevinylene–*m*-phenylene–vinylene–phenylene or the pair of polyphenoxy branch chains 3',5'-substituted on the outer-phenyl ring. However, the NBMOs are confinable to separate regions at the biphenyl linkage or between the inner 1,3,5-benzene core and the outer-phenyl rings, and a reduced exchange interaction between unpaired electrons in the biradical through the inner central core minimizes the stability of a multiplet ground state.

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Chart 1

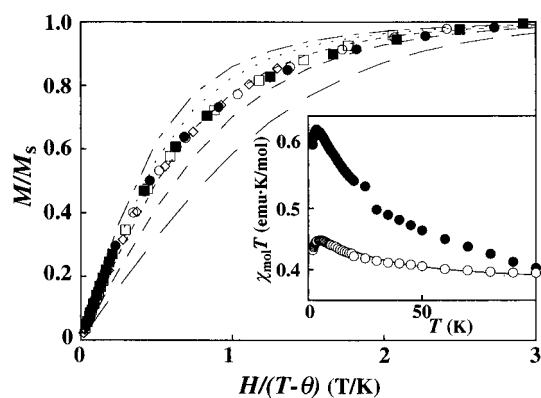
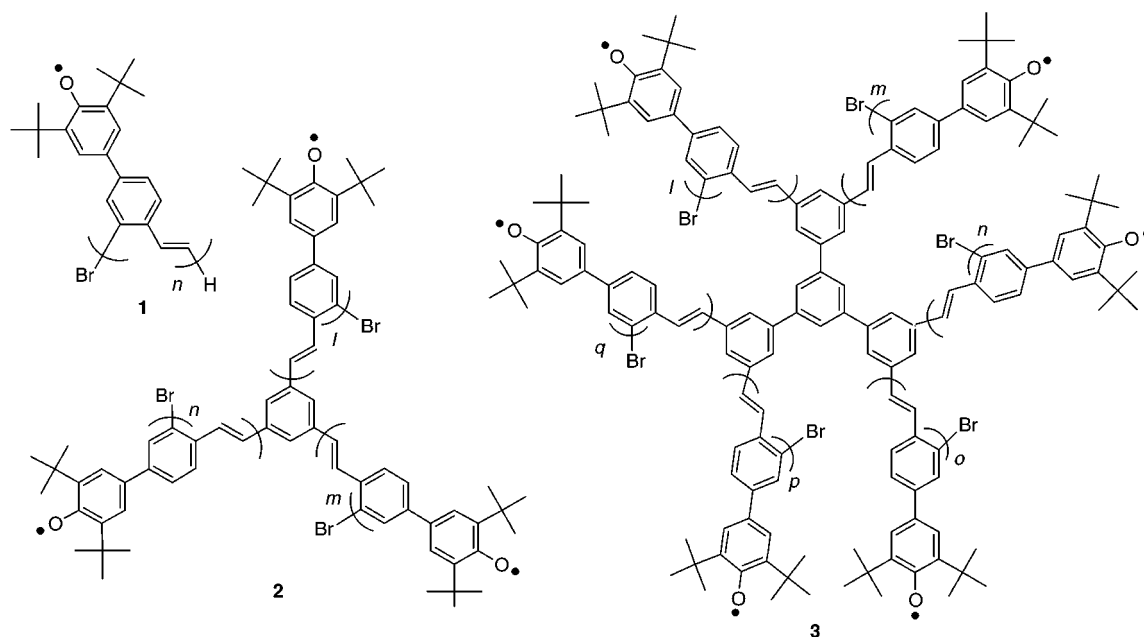
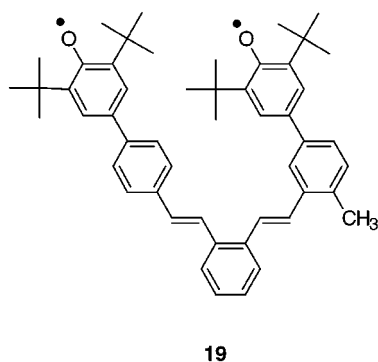


Figure 5. M/M_s vs $H/(T - \theta)$ plots of the polyradical **3** with DP = 34 and spin concn = 0.63 spin/unit in frozen 2Me-THF at $T = 1.8$ (●), 2.0 (■), 2.5 (○), 3 (□), and 5 (◇) K, and the theoretical curves corresponding to the $S = 1/2, 2/2, 3/2, 4/2,$ and $5/2$ Brillouin functions. Inset: $\chi_{\text{mol}}T$ vs T plots (●) of the polyradical **3** and (○) of the hexaradical **18** with spin concn = 0.88 spin/unit in frozen 2Me-THF. Solid line is a theoretical curve calculated using eq 1 for **18** ($2J = 19 \text{ cm}^{-1}, \theta = -0.05 \text{ K}, x_1 = 0.39, x_2 = 0.61, x_3 = 0$).

Chart 2



Conclusion

Pendant-type polyphenoxyl attached to poly(1,2-phenylenevinylene) **1** was extended to star-shaped homo-

logues, **2** and **3**, through a simple one-pot polymerization. The polyradicals were chemically stable and easily handled even at room temperature. The three-branched polyradical **2** based on the core of 1,3,5-benzene displayed an average S of 7/2 to 8/2, while S remained at 3/2 to 4/2 for the six-branched polyradical **3** based on 1,3,5-tris(3',5'-disubstituted phenyl)benzene. A simple coupler of 1,3,5-benzene was sufficient to ferromagnetically connect the polyphenoxyl branch chains. The high-spin state of **2** at low temperature was not sensitive to a spin defect in **2**, and S increased with the molecular size of **2**. Because **2** still possesses the bromide sites at the end of each branch chain, it can be effectively used for the purpose of synthesizing a three-dimensional and starburst-shaped further extension of the high-spin polyphenoxyl.

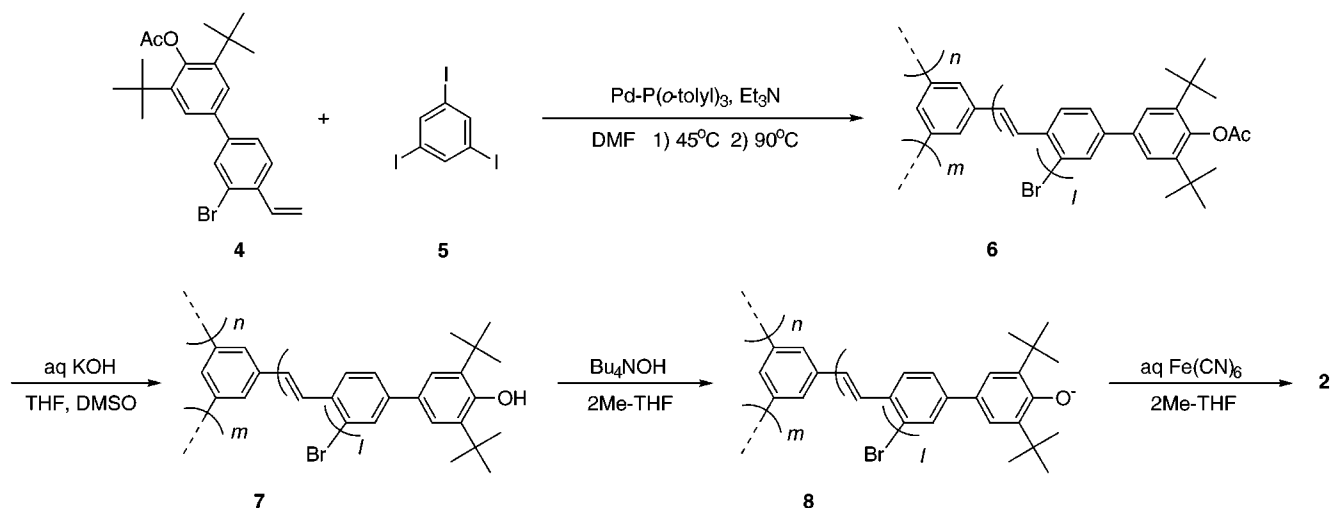
Experimental Section

1,3,5-Triiodobenzene (5). **5** was prepared via the direct iodination of *p*-nitroaniline, deamination, reduction of the nitro group, and diaziodination: mp 183 °C (184 °C in lit.¹²); MS (m/z), 455 (M^+), calcd for $M = 455.8$; $^1\text{H NMR}$ (CDCl_3 , 500 MHz; ppm) δ 7.00 (s, 3H, phenyl); $^{13}\text{C NMR}$ (CDCl_3 , ppm) δ 95.20, 144.42.

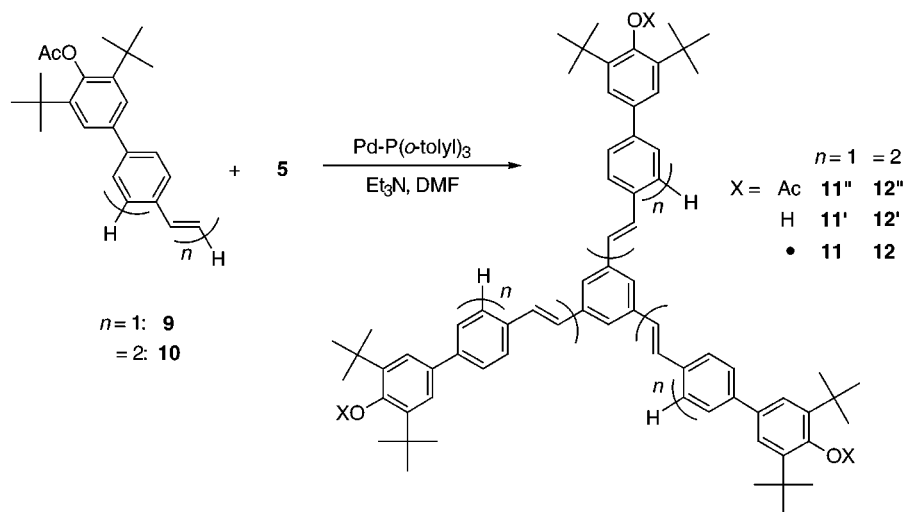
1,3,5-Tris[poly(4-(3',5'-di-*tert*-butyl-4'-acetoxyphe-nyl)-1,2-phenylenevinylene)]benzene (6). Palladium acetate (138 mg, 0.6 mmol), tri-*o*-tolylphosphine (375 mg, 1.2 mmol), triethylamine (3.12 g, 3.08 mmol), and **5** (46.0 mg, 0.1 mmol) were added to a DMF solution (12.3 mL) of the 2-bromo-4-(3',5'-di-*tert*-butyl-4'-acetoxyphe-nyl)styrene (**4**) (see ref 5) (2.6 g, 6.06 mmol) (molar feed ratio $4/5 = 60$). The solution was warmed at 45 °C for 6 h and then heated to 90 °C for 18 h. The mixture was separated using a polystyrene-gel column with CHCl_3 eluent and was purified by reprecipitation from CHCl_3 in methanol to yield the polymer as a yellow powder: yield 42%; IR (KBr pellet, cm^{-1}) 1765 ($\nu_{\text{C=O}}$), 960 ($\delta_{\text{transHC=CH}}$); $^1\text{H NMR}$ (CDCl_3 , 500 MHz; ppm) δ 1.35 (s, 54H, *tert*-butyl), 2.32 (s, 9H, $-\text{O}-\text{CO}-\text{CH}_3$), 7.03–8.08 (m, 24H, Ar, $\text{CH}=\text{CH}$); $^{13}\text{C NMR}$ (CDCl_3 , ppm) δ 22.53 (CH_3), 31.98, 36.20 (*t*-Bu), 125.85, 127.40, 127.72, 128.05, 129.18, 129.39, 132.11, 135.97, 137.66, 138.45, 138.67, 142.17, 143.68, 147.68 (aromatic), 170.76 (Ac). The 14 peaks based on aromatic carbons were assigned to the small letter numbers 3, 12, 11, 6, 8, 7, 13, 2,

(12) Willgerodt, A. *Berichte* **1901**, *34*, 3347.

Scheme 1



Scheme 2



4, 14, 10, 9, 5, and 1, respectively, in **6** in Chart 4. Anal. Calcd for $(C_{24n}H_{28n}Br_3O_{2n})C_6H_3$ ($n = 68$): C, 81.97; H, 7.95; Br, 1.00. Found: C, 81.95; H, 7.92; Br, 1.00; I, <0.01. The polymerization was carried out under the 4/5 feed ratio of 45 or 30 to obtain the polymer with a different molecular weight: yield 45 and 48%, respectively (see Table 1).

1,3,5-Tris[poly(4-(3',5'-di-*tert*-butyl-4'-hydroxyphenyl)-1,2-phenylenevinylene)]benzene (7). **6** (207 mg) was dissolved in a small amount of THF. To its suspension in DMSO (47 mL) was added 2.5 N KOH (2.3 mL), and 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 **7**: yield 48%; IR (KBr pellet, cm^{-1}) 3640 (ν_{O-H}), 960 ($\delta_{transHC=CH}$); 1H NMR ($CDCl_3$, 500 MHz; ppm) δ 1.45 (s, 54H *tert*-butyl), 5.24 (s, 3H, OH), 7.39–7.78 (m, 24H, Ar, CH=CH); ^{13}C NMR ($CDCl_3$, ppm) δ 29.85, 33.96, 123.43, 123.55, 126.25, 126.51, 126.78, 127.64, 128.12, 131.66, 133.68, 134.72, 135.78, 136.12, 141.44, 153.17. The molecular weight of the polymer was measured by a light-scattering molecular weight analyzer (Tosoh LS-8000): mol wt = 2.1×10^4 (DP = 70). Anal. Calcd for $(C_{22n}H_{26n}Br_3O_n)C_6H_3$ ($n = 68$): C, 85.33; H, 8.38; Br, 1.14. Found: C, 85.29; H, 8.42; Br, 1.14; I, <0.01.

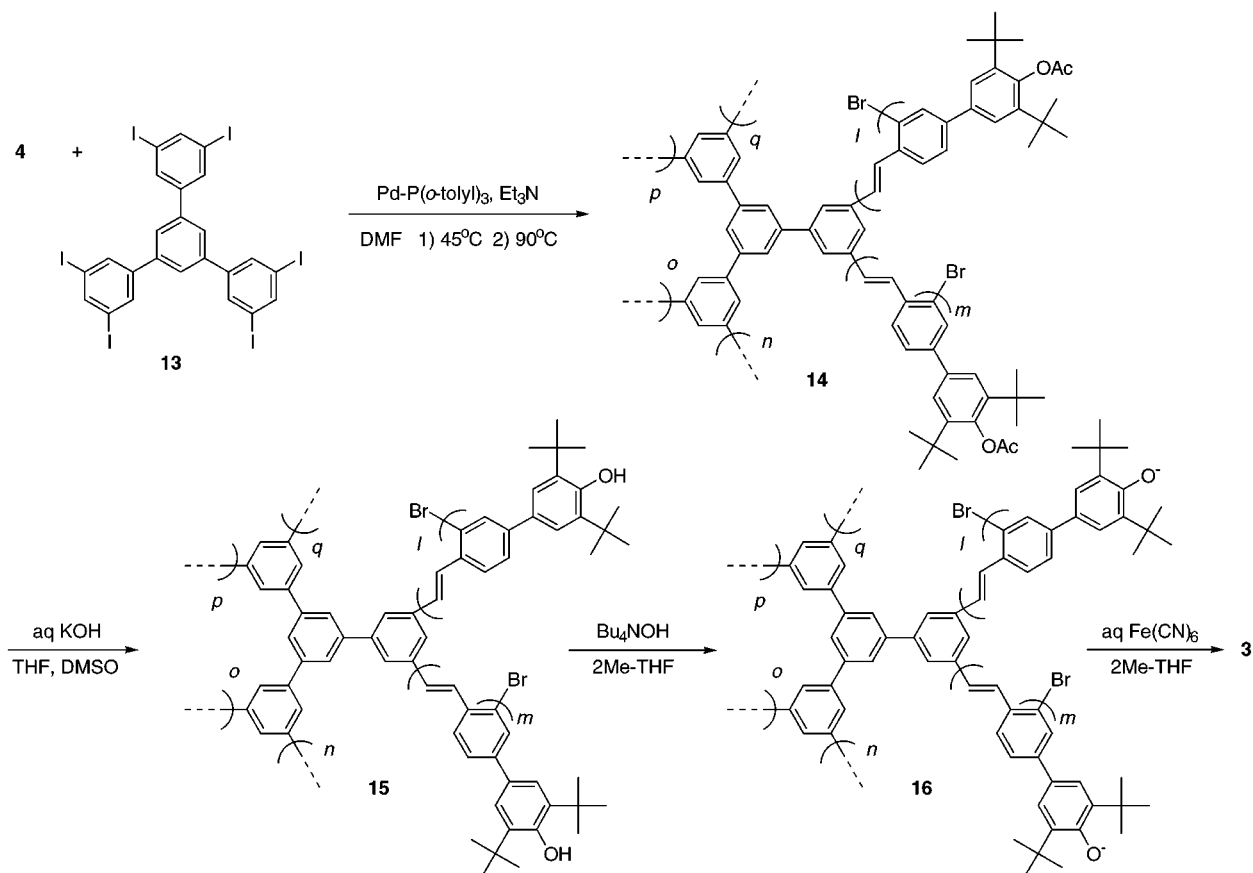
4-(3',5'-Di-*tert*-butyl-4'-acetoxyphenyl)styrene (9). A 3,5-di-*tert*-butyl-4-acetoxyphenyl group was introduced to *p*-bromotoluene via the Grignard coupling reaction with (3,5-di-*tert*-butyl-4-trimethylsilyloxyphenyl)magnesium bromide using [1,3-bis(diphenylphosphino)propane]nickel(II) as a catalyst.

The protecting trimethylsilyl group was then changed to an acetyl group, and the methyl group was converted to a vinyl group via a Wittig reaction: total yield 35%; IR (KBr pellet, cm^{-1}) 1755 ($\nu_{C=O}$), 1628 ($\delta_{C=C}$); 1H NMR ($CDCl_3$, 500 MHz; ppm) δ 1.42 (s, 18H *tert*-butyl), 2.37 (s, 3H, $-O-CO-CH_3$), 5.25 (d, 1H, 10 Hz, $-CH=CH_2$), 5.77 (d, 1H, 17 Hz, $-CH=CH_2$), 6.75 (dd, 1H, 10 Hz, 17 Hz, $-CH=CH_2$), 7.21–7.52 (m, 6H, Ar, CH=CH); ^{13}C NMR ($CDCl_3$, ppm) δ 22.70, 31.48, 35.54, 113.76, 125.25, 126.52, 127.40, 136.39, 136.42, 137.82, 141.00, 142.55, 147.56, 171.14; MS (m/z) 350 (M^+), calcd for $M = 350.2$.

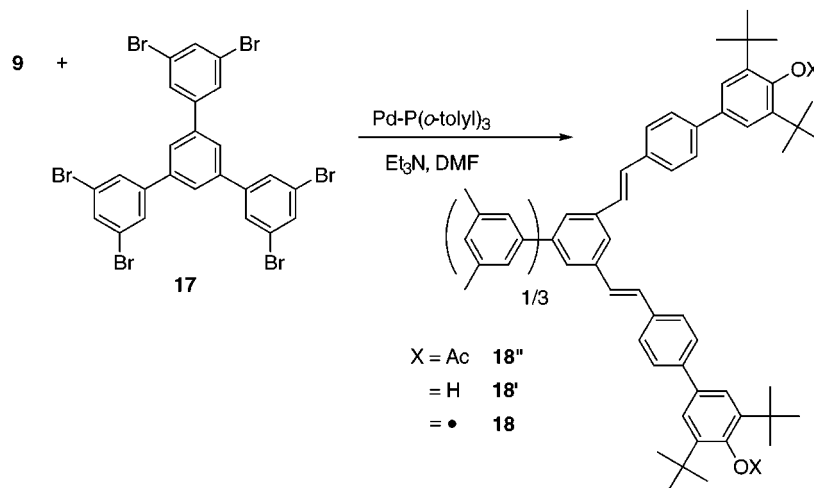
2-Vinyl-5,4'-bis(3,5-di-*tert*-butyl-4'-acetoxyphenyl)stilbene (10). 2-Methyl-5,4'-bis(3,4-di-*tert*-butyl-4'-acetoxyphenyl)stilbene was prepared by coupling 2-bromo-4-(3',5'-di-*tert*-butyl-4'-acetoxyphenyl)toluene with **9** via the Heck reaction. Palladium acetate (215 mg, 0.958 mmol), tri-*o*-tolylphosphine (583 mg, 1.92 mmol), and triethylamine (4.86 g, 47.9 mmol) were added to a 0.5 M DMF (19.2 mL) solution of the 2-bromo-4-(3',5'-di-*tert*-butyl-4'-acetoxyphenyl)toluene (2.0 g, 4.84 mmol) and **9** (1.7 g, 4.84 mmol) and stirred for 12 h at 90 °C: yield 60%; mp 127–128 °C; IR (KBr pellet, cm^{-1}) 1765 ($\nu_{C=O}$), 962 ($\delta_{transHC=CH}$); 1H NMR ($CDCl_3$, 500 MHz; ppm) δ 1.41 (s, 36H, *tert*-butyl), 2.38 (s, 6H, $-O-CO-CH_3$), 2.84 (s, 3H, $-CH_3$), 7.07–7.76 (m, 13H, Ar, CH=CH); ^{13}C NMR ($CDCl_3$, ppm) δ 19.66, 22.73, 31.54, 35.60, 124.60, 125.26, 125.44, 126.66, 126.79, 126.99, 127.58, 130.05, 130.76, 134.72, 136.50, 136.81, 137.81, 138.42, 139.93, 140.92, 142.66, 142.77, 147.46, 147.65, 171.20; MS (m/z) 686 (M^+), calcd for $M = 686.4$. Anal. Calcd for $C_{47}H_{58}O_4$: C, 82.17; H, 8.51. Found: C, 82.22; H, 8.52.

N-Bromosuccinimide (475 mg, 2.67 mmol) and AIBN were

Scheme 3



Scheme 4



suspended in the CCl_4 solution (25 mL) of 2-methyl-5,4'-bis-(3,5-di-*tert*-butyl-4'-acetoxyphenyl)stilbene (1.83 g, 2.67 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 (25 mL) and triphenylphosphine (0.70 g, 2.67 mmol) were added, and the solution was stirred at 50 °C for 6 h. The solution was poured into diethyl ether to give the phosphonium salt (1.68 g): yield 61%.

The phosphonium salt (1.5 g, 1.46 mmol) was suspended in 25% formaldehyde (15 mL), and 5 N NaOH (3 mL) was added dropwise. The mixture was stirred for 1 h and extracted with ether and then evaporated. The crude product was purified by silica gel-column separation with hexane/ CHCl_3 eluent to yield **10**: yield 60%; mp 111–112 °C; IR (KBr pellet, cm^{-1}) 1765 ($\nu_{\text{C=O}}$), 962 ($\delta_{\text{transHC=CH}}$); ^1H NMR (CDCl_3 , 500 MHz; ppm)

δ 1.41 (s, 36H, *tert*-butyl), 2.37 (s, 6H, $-\text{O}-\text{CO}-\text{CH}_3$), 5.39 (d, 1H, 10 Hz, $-\text{CH}=\text{CH}_2$), 5.74 (d, 1H, 16 Hz, $-\text{CH}=\text{CH}_2$), 7.13 (dd, 1H, 10 Hz, 16 Hz, $-\text{CH}=\text{CH}_2$), 7.41–7.73 (m, 13H, Ar, $\text{CH}=\text{CH}$); ^{13}C NMR (CDCl_3 , ppm) δ 14.11, 22.65, 31.50, 35.57, 116.52, 125.22, 125.37, 125.44, 126.58, 126.78, 126.94, 126.99, 127.58, 131.10, 134.63, 135.24, 135.98, 136.31, 137.76, 138.01, 140.98, 141.36, 142.55, 142.73, 147.63, 147.66, 171.11; MS (m/z) 698 (M^+), calcd for $\text{M} = 698.4$. Anal. Calcd for $\text{C}_{48}\text{H}_{58}\text{O}_4$: C, 82.48; H, 8.36. Found: C, 82.45; H, 8.38.

1,3,5-Tris[4'-(3'',5''-di-*tert*-butyl-4''-acetoxyphenyl)styryl]benzene (11''). 1,3,5-Tris[4'-(3'',5''-di-*tert*-butyl-4''-acetoxyphenyl)styryl]benzene (**11''**) was prepared via the same Heck reaction. Palladium acetate (213 mg, 0.950 mmol), tri-*o*-tolylphosphine (579 mg, 1.90 mmol), and triethylamine (4.81 g, 47.6 mmol) were added to a 0.5 M DMF (19.0 mL) solution of **9** (2.5 g, 7.13 mmol) and **5** (1.01 g, 2.23 mmol) (**9/5** = 3.2):

Chart 3

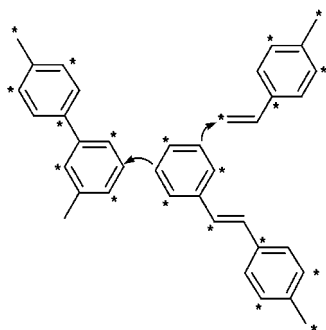
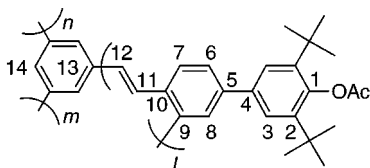


Chart 4



yield 63%; IR (KBr pellet, cm^{-1}) 1765 ($\nu_{\text{C=O}}$), 960 ($\delta_{\text{transHC=CH}}$); $^1\text{H NMR}$ (CDCl_3 , 500 MHz; ppm) δ 1.42 (s, 54H, *tert*-butyl), 2.38 (s, 9H, $-\text{O}-\text{CO}-\text{CH}_3$), 7.22–7.74 (m, 27H, Ar, $\text{CH}=\text{CH}$); $^{13}\text{C NMR}$ (CDCl_3 , ppm) δ 22.68, 31.50, 35.58, 125.21, 126.98, 127.60, 128.30, 129.09, 136.05, 137.74, 138.33, 140.99, 142.10, 142.73, 147.64, 171.12; FAB-MS (m/z) 1122.8 (M^+), calcd for $\text{M} = 1122.7$. Anal. Calcd for $\text{C}_{78}\text{H}_{90}\text{O}_6$: C, 83.38; H, 8.07. Found: C, 83.40; H, 8.10.

11'' (0.737 g, 0.66 mmol) was dissolved in a small amount of THF. To its suspension in DMSO (71.5 mL) was added 2.5 N KOH (3.6 mL), and 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 and was evaporated to give 1,3,5-tris[4'-(3'',5''-di-*tert*-butyl-4''-hydroxyphenyl)styryl]benzene (**11'**): yield 73%; IR (KBr pellet, cm^{-1}) 3636 ($\nu_{\text{O-H}}$), 960 ($\delta_{\text{transHC=CH}}$); $^1\text{H NMR}$ (CDCl_3 , 500 MHz; ppm) δ 1.45 (s, 54H, *tert*-butyl), 5.26 (s, 3H, OH), 7.19–7.76 (m, 27H, Ar, $\text{CH}=\text{CH}$); $^{13}\text{C NMR}$ (CDCl_3 , ppm) δ 31.53, 34.57, 123.84, 126.41, 127.20, 127.98, 129.09, 132.13, 135.48, 136.33, 138.37, 140.80, 141.74, 153.92; FAB-MS (m/z) 996.2 (M^+), calcd for $\text{M} = 996.6$. Anal. Calcd for $\text{C}_{72}\text{H}_{84}\text{O}_3$: C, 86.70; H, 8.49. Found: C, 86.66; H, 8.47.

1,3,5-Tris[2'-styryl-{4',5''-bis(3,5-di-*tert*-butyl-4-acetoxyphenyl)stilbene}]benzene (12''**)**. 1,3,5-Tris[2'-styryl-{4',5''-bis(3,5-di-*tert*-butyl-4-acetoxyphenyl)stilbene}]benzene was prepared in the same manner via the Heck reaction; **10** (6.3 equiv) and **5** (1 equiv): yield 63%; IR (KBr pellet, cm^{-1}) 1765 ($\nu_{\text{C=O}}$), 962 ($\delta_{\text{transHC=CH}}$); $^1\text{H NMR}$ (CDCl_3 , 500 MHz; ppm) δ 1.32 (s, 108H, *tert*-butyl), 2.38 (s, 18H, $-\text{O}-\text{CO}-\text{CH}_3$), 7.22–7.82 (m, 48H, Ar, $\text{CH}=\text{CH}$); $^{13}\text{C NMR}$ (CDCl_3 , ppm) δ 22.54, 22.68, 31.43, 35.59, 124.52, 125.22, 125.37, 125.44, 126.58, 126.78, 126.94, 126.99, 127.58, 129.18, 130.51, 131.12, 134.63, 135.24, 135.98, 136.31, 137.76, 138.01, 140.98, 141.36, 142.55, 142.73, 147.43, 147.67, 171.03, 171.11; FAB-MS (m/z) 2169 (M^+), calcd for $\text{M} = 2169$. Anal. Calcd for $\text{C}_{150}\text{H}_{174}\text{O}_{12}$: C, 83.06; H, 8.09. Found: C, 83.04; H, 8.07.

12'' was deprotected in an alkaline solution to yield 1,3,5-tris[2'-styryl-{4',5''-bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)stilbene}]benzene (**12'**): yield 68%; IR (KBr pellet, cm^{-1}) 3640 ($\nu_{\text{O-H}}$), 961 ($\delta_{\text{transHC=CH}}$); $^1\text{H NMR}$ (CDCl_3 , 500 MHz; ppm) δ 1.47 (s, 108H, *tert*-butyl), 5.27 (s, 6H, OH), 7.08–7.86 (m, 48H, Ar, $\text{CH}=\text{CH}$); $^{13}\text{C NMR}$ (CDCl_3 , ppm) δ 30.55, 34.46, 123.84, 124.03, 124.13, 124.60, 125.77, 126.44, 126.81, 127.20, 127.98, 129.09, 130.38, 131.11, 132.13, 134.45, 135.36, 135.48, 136.17, 136.33, 136.45, 138.37, 140.80, 141.74, 153.34, 153.67; FAB-MS (m/z) 1913 (M^+), calcd for $\text{M} = 1913$. Anal. Calcd for $\text{C}_{138}\text{H}_{162}\text{O}_6$: C, 86.47; H, 8.52. Found: C, 86.43; H, 8.53.

1,3,5-Tris(3',5'-diiodophenyl)benzene (13**)**. 1,3,5-Triiodobenzene (10.4 g, 22.9 mmol) was dissolved in a dry diethyl ether (450 mL), and the solution was cooled at –78 °C. To

this solution was added *n*-butyllithium (14.3 mL of a 1.6 M hexane solution, 22.9 mmol), the mixture was stirred for 1 h at –78 °C, and then *N,N*-dimethylacetamide (2.19 g, 25.1 mmol) was added dropwise. The solution was allowed to warm to ambient temperature overnight. The reaction was quenched with dilute HCl (10%, 145 mL) and then extracted with CHCl_3 . After evaporation, the orange crude product was purified by recrystallization from ethanol to give 3,5-diiodoacetophenone as a white crystal: yield 44%; mp = 124–125 °C; IR (KBr pellet, cm^{-1}) 1685 ($\nu_{\text{C=O}}$); $^1\text{H NMR}$ (CDCl_3 , 500 MHz; ppm) δ 2.55 (s, 3H, CH_3), 8.21 (d, 2H, Ph), 8.23 (t, 1H, Ph); $^{13}\text{C NMR}$ (CDCl_3 , ppm) δ 26.5, 95.0, 136.5, 139.9, 149.3, 195.1; MS (m/z) 372 (M^+), calcd for $\text{M} = 371.9$.

The solid mixture of 3,5-diiodoacetophenone (1.1 g, 2.96 mmol), concentrated H_2SO_4 (53.2 mg, 0.543 mmol), and $\text{K}_2\text{S}_2\text{O}_7$ (0.96 g, 3.84 mmol) was heated to 180 °C for 12 h. The brownish crude was purified by recrystallization from CHCl_3 to give **13** as a white needle crystal: yield 32%; mp 427–429 °C; $^1\text{H NMR}$ (CDCl_3 , 500 MHz; ppm) δ 7.58 (bs, 3H, Ph), 7.92 (bs, 6H, Ph), 8.22 (bs, 3H, Ph); $^{13}\text{C NMR}$ (CDCl_3 , ppm) δ 98.8, 123.4, 129.2, 140.3, 145.6, 149.8; MS (m/z) 1062 (M^+), calcd for $\text{M} = 1061.7$.

1,3,5-Tris[3',5'-di-poly(4-(3',5'-di-*tert*-butyl-4'-acetoxyphe-nyl)-1,2-phenylenevinylene)]benzene (14**)**. Palladium acetate (132 mg, 0.424 mmol), tri-*o*-tolylphosphine (358 mg, 0.848 mmol), 1,3,5-tris(3',5'-diiodophenyl)benzene (52.3 mg, 48.5 μmol), and triethylamine (2.98 g, 21.2 mmol) were added to a DMF solution (11.7 mL) of the styrene monomer **4** (2.5 g, 5.83 mmol), and the mixture was warmed at 45 °C for 6 h. The mixture was then heated to 90 °C for 18 h. The mixture was separated using a polystyrene-gel column with CHCl_3 eluent and was purified by reprecipitation from CHCl_3 in methanol to yield the polymer as a yellow powder: yield 62%; IR (KBr pellet, cm^{-1}) 1765 ($\nu_{\text{C=O}}$), 961 ($\delta_{\text{transHC=CH}}$); $^1\text{H NMR}$ (CDCl_3 , 500 MHz; ppm) δ 1.36 (s, 108H, *tert*-butyl), 2.34 (s, 18H, $-\text{O}-\text{CO}-\text{CH}_3$), 7.13–7.88 (m, 54H, Ar, $\text{CH}=\text{CH}$); $^{13}\text{C NMR}$ (CDCl_3 , ppm) δ 22.68 (CH_3), 31.48, 35.53 (*t*-Bu), 124.53, 125.16, 125.32, 125.38, 126.57, 126.76, 126.97, 128.31, 128.61, 128.81, 130.32, 131.50, 134.57, 136.56, 137.88, 141.29, 142.69, 147.61 (aromatic), 171.07 (Ac). Anal. Calcd for $(\text{C}_{24n}\text{H}_{28n}\text{Br}_3\text{O}_{2n})\text{C}_{24}\text{H}_{12}$ ($n = 22$): C, 78.52; H, 7.44; Br, 5.69. Found: C, 78.50; H, 7.43; Br, 5.69; I, <0.01.

1,3,5-Tris[3',5'-di-poly(4-(3',5'-di-*tert*-butyl-4'-hydroxyphe-nyl)-1,2-phenylenevinylene)]benzene (15**)**. **14** was deprotected in an alkaline solution to yield the hydroxy precursor **15**: IR (KBr pellet, cm^{-1}) 3640 ($\nu_{\text{O-H}}$), 961 ($\delta_{\text{transHC=CH}}$); $^1\text{H NMR}$ (CDCl_3 , 500 MHz; ppm) δ 1.43 (s, 108H *tert*-butyl), 5.24 (s, 6H, OH), 7.28–7.82 (m, 54H, Ar, $\text{CH}=\text{CH}$); $^{13}\text{C NMR}$ (CDCl_3 , ppm) δ 29.85, 33.96, 123.40, 123.60, 124.76, 126.32, 126.49, 126.75, 127.62, 128.08, 129.43, 131.70, 133.64, 134.71, 135.78, 136.12, 137.32, 141.44, 142.57, 153.17; mol wt = 1.1×10^4 . Anal. Calcd for $(\text{C}_{22n}\text{H}_{26n}\text{Br}_3\text{O}_n)\text{C}_{24}\text{H}_{12}$ ($n = 34$): C, 82.83; H, 8.01; Br, 4.29. Found: C, 82.80; H, 8.04; Br, 4.29; I, <0.01.

1,3,5-Tris(3',5'-dibromophenyl)benzene (17**)**. 3,5-Dibromoacetophenone was prepared in the same method of **13** using 1,3,5-triiodobenzene, to give a white crystal: yield 64%; mp 61–62 °C; IR (KBr pellet, cm^{-1}) 1693 ($\nu_{\text{C=O}}$); $^1\text{H NMR}$ (CDCl_3 , 500 MHz; ppm) δ 2.59 (s, 3H, CH_3), 7.85 (t, 1H, Ar), 8.00 (d, 2H, Ar); $^{13}\text{C NMR}$ (CDCl_3 , ppm) δ 26.6, 123.5, 130.1, 138.2, 139.6, 195.2; MS (m/z) 276 (M^+), 278 ($\text{M}^+ + 2$), 280 ($\text{M}^+ + 4$), calcd for $\text{M} = 277.9$.

The solid mixture of 3,5-dibromoacetophenone (3.9 g, 14.9 mmol), concentrated H_2SO_4 (252 mg, 2.57 mmol), and $\text{K}_2\text{S}_2\text{O}_7$ (4.55 g, 18.2 mmol) was heated to give an off-white solid: yield 36; mp 314–315 °C; $^1\text{H NMR}$ (CDCl_3 , 500 MHz; ppm) δ 7.65 (bs, 3H, Ar), 7.72 (bs, 9H, Ar); $^{13}\text{C NMR}$ (CDCl_3 , ppm) δ 123.5, 125.9, 129.2, 133.4, 140.3, 143.62.

1,3,5-Tris[3',5'-di-{4''-(3''',5''',5''''-di-*tert*-butyl-4'''-acetoxyphe-nyl)styryl}phenyl]benzene (18''**)**. **18''** was prepared via the Heck reaction; **9** (1.42 g, 4.04 mmol) and **17** (0.5 g, 0.64 mmol) were dissolved in a DMF solution (18.7 mL) of palladium acetate (4.74 g, 46.8 mmol), tri-*o*-tolylphosphine (0.1050 g, 93.5 mmol), and triethylamine (0.2849 g, 46.8 mmol), and the mixture was warmed at 90 °C for 18 h: yield 61%; IR

(KBr pellet, cm^{-1}) 1765 ($\nu_{\text{C=O}}$), 962 ($\delta_{\text{transHC=CH}}$); ^1H NMR (CDCl_3 , 500 MHz; ppm) δ 1.40 (s, 108H, *tert*-butyl), 2.36 (s, 18H, $-\text{O}-\text{CO}-\text{CH}_3$), 7.24–8.01 (m, 60H, Ar, $\text{CH}=\text{CH}$); ^{13}C NMR (CDCl_3 , ppm); δ 22.68, 31.50, 35.58, 124.02, 125.03, 125.21, 126.98, 127.60, 128.30, 129.22, 136.03, 137.71, 138.53, 140.99, 142.18, 142.47, 142.66, 171.12; FAB-MS (m/z) 2392 (found), calcd for $\text{M} = 2395$. Anal. Calcd for $(\text{C}_{24}\text{H}_{29}\text{O}_2)_6\text{C}_{24}\text{H}_{12}$: C, 84.17; H, 7.82; Br, 0. Found: C, 83.72; H, 7.76; Br, <0.2.

18'' was deprotected in an alkaline solution to yield 1,3,5-tris[3',5'-di-{4''-(3''',5'''-di-*tert*-butyl-4''-hydroxyphenyl)styryl}-phenyl]benzene (**18'**): yield 85%; ^1H NMR (CDCl_3 , 500 MHz; ppm) δ 1.50 (s, 108H, *tert*-butyl), 5.27 (s, 6H, OH), 7.20–8.10 (m, 60H, Ar, $\text{CH}=\text{CH}$); ^{13}C NMR (CDCl_3 , ppm) δ 30.36, 34.51, 123.85, 124.88, 127.00, 127.22, 127.86, 129.36, 131.98, 135.34, 136.18, 136.28, 138.61, 141.67, 142.13, 142.52, 153.66; FAB-MS (m/z) 2142 (found), calcd for $\text{M} = 2143$. Anal. Calcd for $(\text{C}_{24}\text{H}_{27}\text{O})_6\text{C}_{24}\text{H}_{12}$: C, 87.35; H, 8.18; Br, 0. Found: C, 86.92; H, 8.13; Br, <0.2.

Oxidation. A small excess of (*n*- C_4H_9)₄NOH was added to a 2Me-THF or toluene solution (50 mL) of the hydroxy precursors (0.025 unit mmol) under a nitrogen atmosphere in a glovebox (for the ESR measurement; 2 mL and 0.06 unit mmol, respectively, for SQUID). Then, the solution was vigorously stirred with 10 mL of aqueous $\text{K}_3\text{Fe}(\text{CN})_6$ (2.5 mmol; 10 equiv to the phenolate) at room temperature (1 mL and 0.6 mmol, respectively, for SQUID). The solution rapidly

turned deeply green after 10–20 min, which was ascribed to the radical formation. The organic layer was dried over anhydrous sodium sulfate.

ESR and SQUID Measurements. ESR spectra were taken using a JEOL JES-TE200 ESR spectrometer with 100 kHz field modulation. Spin concentration of each sample was determined both by careful integration of the ESR signal standardized with that of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) solution and by analyzing the saturated magnetization at the SQUID measurement.

The 2Me-THF or toluene solutions of the radicals were 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 100 K at a field of 0.5 T.

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