be regarded as a donor–acceptor complex, as there is no charge separation between the Al units and the bridging iodine atoms are only weakly charged.[9d] $[H_3Al_5I_6]$ (**1c**; C_1 symmetry): $E = -1282.817496$; Al(1)–Al(2) 259.7, Al(1)–Al(3) 259.7, Al(2)–I(3) 291.9, Al(2)–I(4) 305.3, Al(3)–I(3) 292.2, Al(3)–I(4) 305.4, Al(4)–I(4) 268.4, Al(5)–I(3) 282.0, Al(4)–Al(5) 256.4, Al(2)–Al(3) 333.0; Al(2)-Al(1)-Al(3) 79.8, I(4)-Al(4)-Al(5) 114.2, Al(4)-Al(5)-I(3) 100.2; $\delta(H_{Al(4)}) = -0.02$, $\delta(H_{Al(2)}) = 0.09$, $\delta(H_{Al(3)}) = 0.09$, $\delta(Al(1)) = 0.40$, $\delta(Al(2)) = 0.04$, $\delta(Al(3)) = 0.04$, $\delta(Al(4)) = 0.28$, $\delta(Al(5)) = 0.35$, $\delta(I(3)) = -0.03$, $\delta(I(4)) = -0.05$, $\delta(I(5)) = -0.24$, $\delta(\text{“}Al_3\text{”}) = -0.05$, $\delta(\text{“}Al_2\text{”}) = 0.05$; that is, **1c** should be regarded as a donor–acceptor complex, as there is no charge separation between the Al units and the bridging iodine atoms are only weakly charged.[9d] $Al_2I_6 + 3\,AlH \rightarrow H_3Al_5I_6$: $\Delta E = -438\ \text{kJ mol}^{-1}$. $Al_2I_6 + 3\,[CpAl] \rightarrow [Cp_3Al_5I_6]$: $\Delta E = -199\ \text{kJ mol}^{-1}$. a) K. Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, *240*, 283–290; *Chem. Phys. Lett.* **1995**, *242*, 652–660; b) R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* **1989**, *162*, 165–169; c) A. Schäfer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, *97*, 2571–2577. d) A similar polarization was also calculated for Al_2I_6: donor-acceptor complex; D_{2h} symmetry; $Al-I_{bridge}$ 270.7, $Al-I_{terminal}$ 250.2, Al–Al 367.8; $\delta(I_{bridge}) = -0.05$, $\delta(I_{terminal}) = -0.21$; $\delta(Al) = 0.47$.

[10] a) A. Ecker, E. Baum, M. A. Friesen, M. A. Junker, C. Üffing, R. Köppe, H. Schnöckel, *Z. Anorg. Allg. Chem.* **1998**, *624*, 513–516; b) A. Ecker, H. Schnöckel, *Z. Anorg. Allg. Chem.*, in press.

[11] In the ^{27}Al NMR spectrum, monomeric [Cp*Al] can only be identified in equilibrium with $[\{Cp^*Al\}_4]$ above about 60 °C, because the energy for the tetramerization to $[\{Cp^*Al\}_4]$ is around $-150\ \text{kJ mol}^{-1}$.[1]

[12] The NMR spectrum of a mixture of $[\{Cp^*Al\}_4]$ and Al_2I_6 in deuterated toluene shows signals at the following shifts: ^{1}H NMR (Bruker AC-250 spectrometer (250.134 MHz); room temperature; reference: $\delta(C_7D_7H)$): $\delta = 2.09$; ^{27}Al NMR (Bruker AMX-300 spectrometer; room temperature; external reference: $\delta([Al(H_2O)_6]^{3+})$): $\delta = 0$. After a reaction period of a few days at -20 °C: ^{1}H NMR: δ ($\omega_{1/2}$[Hz]) = 2.07 (10), 2.03 (10) (both with low intensity), 1.93 (2), 1.85 (3), 1.78 (3), 1.60 (3) (the latter in a ratio of about 3:3:2); ^{27}Al NMR: δ ($\omega_{1/2}$[Hz]) = 110 (br, weak), -21 (550), -83 (260). After about one month at -20 °C: ^{1}H NMR: δ ($\omega_{1/2}$[Hz]) = 1.85 (2), 1.74 (2), 1.60 (2) (in a ratio of about 2:3:4); ^{27}Al NMR: δ ($\omega_{1/2}$[Hz]) = 110 (br, weak), -21 (520), -82 (260). After about three months and intermediate tempering at 120 °C: ^{1}H NMR: δ ($\omega_{1/2}$[Hz]) = 1.57 (sharp, s); ^{27}Al-NMR: δ ($\omega_{1/2}$[Hz]) = -19 (500, weak), -81 (360), -114 (very weak, $[Cp^*_2Al]^+$).[2a] These NMR spectroscopic results indicate a more complex reaction sequence than for the reaction between $[\{Cp^*Al\}_4]$ and $AlCl_3$.[2a]

[13] See, for example, the electrochemical reduction of Al^{III} species to elemental aluminum or the preparation of simple organic aluminum(III) compounds from aluminum and alkyl halides: K. Ziegler, H. Lehmkuhl, *Z. Anorg. Allg. Chem.* **1956**, *283*, 414–424; W. Kautek, W. Fromberg, J. A. de Hek, *Metalloberfläche* **1992**, *46*, 67–74; J. Fischer, *Metalloberfläche* **1996**, *50*, 183–184; A. Ecker, H. Schnöckel, *VDI-Nachrichten* **1996**, *50*, 22; H. Köhnlein, H. Schnöckel, *Aluminum* **1997**, *73*, 766–767.

[14] Additional Al^{III} species are formed by their subsequent disproportionation. This should lead to an increase in the reaction rate for the formation of the desired end products.

Average Octet Radical Polymer: A Stable Polyphenoxyl with Star-Shaped π Conjugation[**]

Hiroyuki Nishide,[*] Makoto Miyasaka, and
Eishun Tsuchida

The search for syntheses of organic molecules with very high spin resulting from intramolecular through-bond magnetic ordering is driven by the desire to realize magnetism based purely on organic components.[1] High-spin alignment in the ground state has been demonstrated for cross-conjugated polyradicals or radical polymer main chains, such as poly(1,3-phenylenecarbene)[1b] and poly(1,3-phenylenephenylmethine).[1c] Pseudo-two-dimensional branched, cyclic, and ladder homologues have also been synthesized to increase the spin quantum number S at low temperature.[2] The aim was to diminish the damage of a radical or spin defect, which is fatal for the cross-conjugated polyradicals. In addition, these polyradicals lacked chemical stability at room temperature.

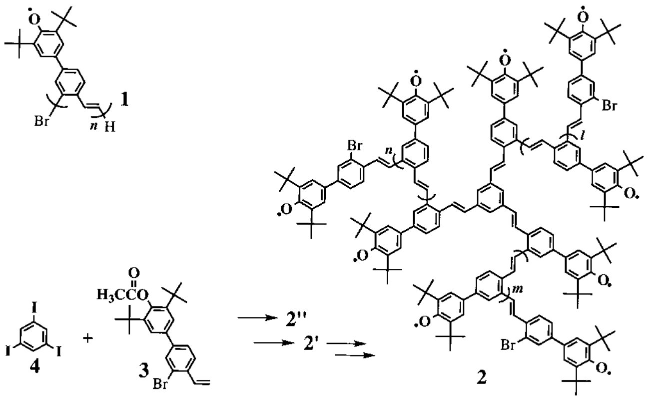
There is another approach to the high-spin molecules that makes use of π-conjugated linear polymers bearing pendant radical groups on the polymer backbone which are π-conjugated with the backbone to ensure the ferromagnetic connectivity of the radicals.[1e] In this type of polyradical, the spin alignment between the pendant unpaired electrons is not sensitive to a spin defects, which are unavoidable for radical polymers of increasing molecular size because the magnetic interaction is transmitted through the π-conjugated polymer backbone. A further advantage is that the pendant, built-in radical groups could be chosen from a series of chemically stable organic radicals. We recently synthesized poly(1,2-phenylenevinylene) containing di-*tert*-butylphenoxyl as the pendant radical group (**1**) which has a through-conjugated backbone bond and allows long-range ferromagnetic exchange interaction between the pendant unpaired electrons: With a spin concentration of 0.7 per monomer unit, **1** displays values for S of 4/2 to 5/2.[3] We report here our successful improvement of both S and the stability of the polyradical by extending **1** to the star-shaped homologue **2** (Scheme 1).

The precursor acetoxypolymer **2″** was synthesized in a one-pot reaction by the Pd-catalyzed Heck reaction of styrene **3** with 1,3,5-triiodobenzene (**4**), the core of the star-shaped polymer (see the Experimental Section). The molecular weight and degree of polymerization ($DP = l + m + n + 6$ for **2**) of the star-shaped polymer was controlled by the feed ratio of **3** to **4** during the polymerization. The iodide groups had completely reacted in every polymer. The DP measured by

---

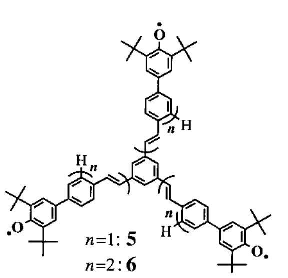
[*] Prof. H. Nishide, M. Miyasaka, Prof. E. Tsuchida
Department of Polymer Chemistry
Waseda University, Tokyo 169-8555 (Japan)
Fax: (+81) 3-3209-5522
E-mail: nishide@mn.waseda.ac.jp

[**] This work was partially supported by Grants-in-Aid for Scientific Research (nos. 277/08246101 and 09305060) from the Ministry of Education, Science and Culture, Japan, and by the NEDO R&D Project on Precision Polycondensation. The authors thank Prof. A. Rajca (University of Nebraska) for his productive comments on this study.



Scheme 1.

light scattering was in agreement with the final bromide content determined by elemental analysis, which supports a linear structure of the side chains. Fourteen peaks in the ^{13}C NMR spectrum, which could be ascribed to the benzene rings and vinylene groups, supported both the head-to-tail linkage structure of the side chains and the 1,3,5-trisvinylene-substituted benzene structure of the core. Polymer **2''** was completely hydrolyzed to the corresponding hydroxypolymer **2'**. Tri- and hexaradical compounds **5** and **6** were also synthesized.



With a small excess of nBu$_4$NOH in 2-methyltetrahydrofuran (2Me-THF), hydroxypolymer **2'** (DP = 33, 42, 70) was converted into the phenolate polymer, which was then heterogeneously oxidized with an aqueous solution of $K_3[FeCN_6]$ to yield the polyradical **2**. This polyradical is also soluble in common solvents such as benzene, THF, and chloroform. The UV absorption was shifted bathochromically to $\lambda_{max} = 450$ nm relative to those of **5**, **6**, and **1** ($\lambda_{max} = 420, 423$, and 425 nm, respectively), which suggested π conjugation in the backbone of **2**.

A solution of **2** in chloroform was cast under an oxygen-free atmosphere to yield a transparent, brown-green, brittle film; the glassy property[4] is ascribed to the rigid structure of **2**. In the solid state **2** is stable even at room temperature. The half-life of the radicals **2**, **1**, and **3** was 3.4, 1.2, and 0.1 d, respectively. The conjugation with and/or the relatively planar skeleton structure of the star-shaped backbone improved the chemical stability of the pendant phenoxyl radical in **2**.

The ESR spectrum of **2** at a low spin concentration shows a broad hyperfine structure at $g = 2.004(2)$, which is attributed to the 5–7 protons of the phenoxyl ring and phenylenevinylene backbone. The distribution of spin density into the core of **2** was indicated by the hyperfine structure of the core model compound **5** at a low spin concentration (Figure 1 a). These ESR results suggested an effectively delocalized spin distribution over the entire star-shaped polyradical, most likely because of its sterically less hindered or relatively planar structure. The ESR spectra of frozen glasses in toluene of **2**, **5**, and **6** with a high spin concentration showed a $\Delta M_s = \pm 2$ forbidden transition ascribed to a triplet species at $g = 4.021(8)$ (Figure 1 b).

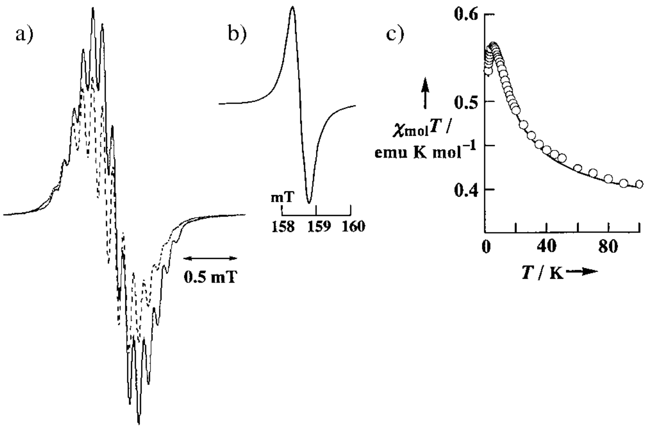


Figure 1. a) ESR spectrum of the core model compound **5** at a low spin concentration in toluene at room temperature (the dashed line represents the simulation, $a_H = 0.10$, 0.09, and 0.08 mT) b) ESR $\Delta M_s = \pm 2$ signal of **5** at a high spin concentration at 77 K. c) Plot of $\chi_{mol}T$ versus T for **5** (spin concentration 0.9) in 2Me-THF. The solid line is the theoretical curve calculated with Equation (1) for $2J = 19\ \mathrm{cm}^{-1}$, $\theta = -0.29$ K, $x_1 = 0$, $x_2 = 0.13(2)$, and $x_3 = 0.86(8)$.[5]

Static magnetic susceptibility and magnetization of the polyradicals in frozen 2Me-THF or toluene were measured with a SQUID magnetometer (Quantum Design MPMS-7). The magnetization plots of triradical **5** were presented close to the Brillouin curve for $S = 3/2$ at temperatures lower than 3 K and indicated a quartet ground state of the triradical. Figure 1 c shows a plot of the product of molar magnetic susceptibility χ_{mol} and T versus T for **5**: as in the case for ferromagnetic species, $\chi_{mol}T$ increases at low temperature from the theoretical value ($\chi_{mol}T = 0.375$) for $S = 1/2$, which was analyzed using the van Vleck expression[5] [Eq. (1)] to obtain the spin exchange coupling constant (J, positive for ferromagnetic compound) of the ferromagnetic interaction. The value $2J = 19 \pm 2\ \mathrm{cm}^{-1}$ for **5** is larger than that ($6 \pm 1\ \mathrm{cm}^{-1}$) for the corresponding diradical analogue 1-[2'-methyl-5-(3'', 5''-di-*tert*-butyl-4''-oxyphenyl)styryl]-2-[4'-(3'',5''-di-*tert*-butyl-4''-oxyphenyl)styryl]benzene. This result indicates that the 1,3,5-benzene core acts as an effective coupler for connecting three polyradical side chains.

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

The inset in Figure 2 gives the $\chi_{mol}T$ plots for the polyradicals **2** and **6**, which have the same spin concentration of about 0.7 and different degrees of polymerization. As is typical of ferromagnetic species, the increase in $\chi_{mol}T$ at low temperature is enhanced for the polyradical with a higher molecular weight; that is, it corresponds to the number of spins in the polyradical molecule. The star-shaped polyradical exhibits a more effective interaction than the corresponding linear polyradical. Figure 2 shows the magnetization M plots for the star-shaped polyradical **2** (DP = 70), normalized with saturated magnetization M_s. The M/M_s curves for **2** even with a spin concentration of 0.80 lie almost on the theoretical

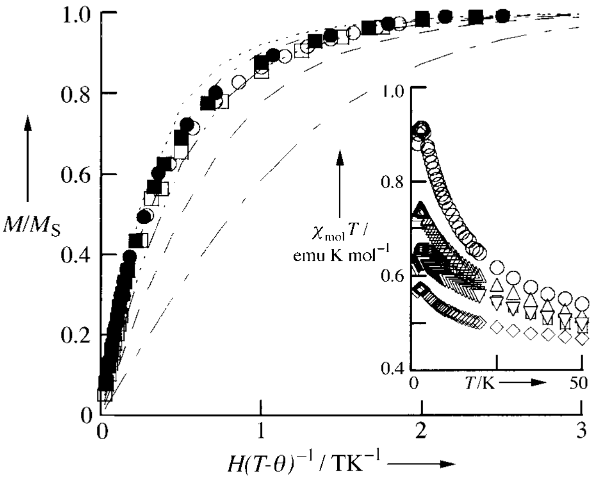


Figure 2. Normalized plots of magnetization M/M_s versus the ratio of magnetic field to temperature for **2** (DP = 70) with a spin concentration 0.80 per monomer unit in 2Me-THF at 1.8 K (●), 2.0 (■), 2.5 (○), and 3 (□) as well as the theoretical curves corresponding to the Brillouin functions for $S = 1/2$, 3/2, 5/2, 7/2, and 9/2. Inset: Plots of $\chi_{mol}T$ versus T for **2** with different degrees of polymerization (DP) and spin concentrations. DP = 70, 0.75 spins/unit (○); DP = 42, 0.68 (△); DP = 33, 0.65 (□). For **1** with DP = 29 and 0.68 spins/unit (▽). For **6** with 0.75 spins/unit (◇).

Brillouin curve for $S = 9/2$ and 6/2 at low and high magnetic field, respectively. This characterizes the polyradical **2** as a mixture of molecular high-spin assemblages[2b, 6] or a disperse spin system with $S = 7/2$ on average.

Experimental Section

Polymerization: Palladium acetate (0.6 mmol), tri-*o*-tolylphosphane (1.2 mmol), 1,3,5-triiodobenzene[7] (0.1 mmol), and triethylamine (3.08 mmol) were added to a solution of monomer **3**[2b] (6.06 mmol) in DMF (12.3 mL). The solution was warmed to 45 °C for 6 h and then heated at 90 °C for 18 h. The mixture was separated on a polystyrene gel column and purified by reprecipitation from chloroform in methanol to yield the polymer as a yellow powder in 42% yield. The molecular weight of the polymer was estimated by a light-scattering measurement (Tosoh LS-8000).

2'': ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.42$ (s, 54H; $C(CH_3)$), 2.38 (s, 9H; $OCOCH_3$), 7.23 – 7.74 (m, 24H; Ar, CH=CH); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 22.53$, 31.98, 36.20, 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, 170.76; IR (KBr): $\tilde{\nu} = 1765$ ($\nu_{C=O}$), 960 cm^{-1} ($\delta_{C=C}$); correct elemental analysis. Iodine content less than 0.01%, as determined by the combustion method. The fluorescence at 450 nm ($\lambda_{ex} = 420$ nm) was ascribed to the *trans*-stilbene structure.

2': Polymer **2''** was converted into **2'** after complete elimination of the protecting acetyl groups with KOH in DMSO/THF. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.45$ (s, 54H; $C(CH_3)$), 5.24 (s, 3H; OH), 7.39 – 7.78 (m, 24H; Ar, CH=CH); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 29.85$, 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; IR (KBr): $\tilde{\nu} = 3640$ (ν_{O-H}), 960 cm^{-1} ($\delta_{C=C}$); $M_n = 2.1 \times 10^4$ ($M_w/M_n = 1.2$) for DP = 70, 1.3×10^4 ($M_w/M_n = 1.2$) for DP = 42, 1.0×10^4 ($M_w/M_n = 1.2$) for DP = 33.

Oxidation: The hydroxypolymer **2'** was completely converted into the phenolate anion with a small excess of nBu$_4$NOH in 2Me-THF and carefully oxidized with an aqueous alkaline solution of $K_3[Fe(CN)_6]$ under an inert atmosphere at room temperature to yield the corresponding polyradicals.

5: 1,3,5-Tris[4'-(3'',5''-di-*tert*-butyl-4''-acetoxyphenyl)styryl]benzene (**5''**) was prepared by the Heck reaction of 4-(3',5'-di-*tert*-butyl-4'-acetoxyphenyl)styrene and **4** in 63% yield. Correct elemental analysis; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.42$ (s, 54H; $C(CH_3)_3$), 2.38 (s, 9H; $OCOCH_3$), 7.22 – 7.74 (m, 27H; Ar, CH=CH); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 22.68$, 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; IR (KBr): $\tilde{\nu} = 1765$ ($\nu_{C=O}$), 960 cm^{-1} ($\delta_{C=C}$); FAB-MS: $m/z = 1122.7$ (found), 1122.7 (calcd). Compound **5''** was deprotected in alkaline solution to yield the hydroxyprecursor **5'**, which was oxidized as described above to give **5**.

6: Compound **6''** was prepared by treating 2-[4'-(3'',5''-di-*tert*-butyl-4''-acetoxyphenyl)styryl]-4-(3',5'-di-*tert*-butyl-4'-acetoxyphenyl)styrene with **4**. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.32$ (s, 108H; $C(CH_3)_3$), 2.38 (s, 18H; $OCOCH_3$), 7.22 – 7.82 (m, 48H; Ar, CH=CH); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 22.54$, 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; IR (KBr): $\tilde{\nu} = 1765$ ($\nu_{C=O}$), 962 cm^{-1} ($\delta_{C=C}$); FAB-MS: $m/z = 2167$ (found), 2167.3 (calcd). Compound **6''** was then deprotected and oxidized to give **6**.

Received: March 26, 1998 [Z11648IE]
German version: *Angew. Chem.* **1998**, *110*, 2497 – 2499

Keywords: EPR spectroscopy · magnetic properties · polymers · polyradicals · radicals

---

[1] a) D. A. Dougherty, *Acc. Chem. Res.* **1991**, *24*, 88 – 94; b) H. Iwamura, N. Koga, *Acc. Chem. Res.* **1993**, *26*, 346 – 351; c) A. Rajca, *Chem. Rev.* **1994**, *94*, 871 – 893; d) J. S. Miller, A. Epstein, *Angew. Chem.* **1994**, *106*, 399 – 429; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 385 – 415; e) H. Nishide, *Adv. Mater.* **1995**, *7*, 937 – 941.

[2] a) N. Nakamura, K. Inoue, H. Iwamura, *Angew. Chem.* **1993**, *105*, 900 – 903; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 872 – 874; b) A. Rajca, S. Utamapanya, *J. Am. Chem. Soc.* **1993**, *115*, 10688 – 10694; c) A. Rajca, K. Lu, S. Rajca, *J. Am. Chem. Soc.* **1997**, *119*, 10335 – 10345; d) A. Rajca, J. Wongsriratanakul, S. Rajca, *J. Am. Chem. Soc.* **1997**, *119*, 11674 – 11686; e) D. Ruiz-Molina, J. Veciana, F. Palacio, C. Rovira, *J. Org. Chem.* **1997**, *62*, 9009 – 9017; f) R. J. Bushby, D. R. McGill, K. M. Ng, N. Taylor, *J. Mater. Chem.* **1997**, *7*, 2343 – 2354.

[3] a) H. Nishide, T. Kaneko, T. Nii, K. Katoh, E. Tsuchida, K. Yamaguchi, *J. Am. Chem. Soc.* **1995**, *117*, 548 – 549; b) H. Nishide, T. Kaneko, T. Nii, K. Katoh, E. Tsuchida, P. M. Lahti, *J. Am. Chem. Soc.* **1996**, *118*, 9695 – 9704.

[4] The polyradical **2** was amorphous and glassy. No glassy → rubbery transition was observed by differential scanning calorimetry up to the thermal decomposition temperature (the temperature for the 10% weight loss was 283 °C under N_2, as measured by thermogravimetry differential thermal analysis (TG-DTA)).

[5] J. H. van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, Oxford University Press, London, **1932**. x_1, x_2, and x_3 are the fractions of the doublet, triplet, and quartet, respectively ($x_1 + x_2 + x_3 = 1$). μ_B is the Bohr magneton, and θ the Weiss constant.

[6] H. Nishide, *ACS Symp. Ser.* **1996**, *644*, 247 – 257.

[7] A. Willgerodt, *Ber. Dtsch. Chem. Ges.* **1901**, *34*, 3347 – 3351.