

## Synthesis of Dendritic, Non-Kekulé-, and Nondisjoint-type Triphenylmethanes Terminated with Galvinoxyl Radicals

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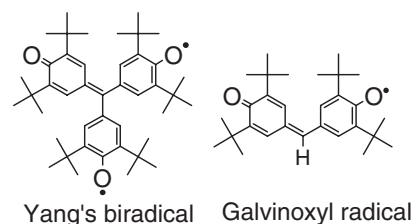
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**ABSTRACT:** A series of triphenylmethanes terminated with (a) hydrogalvinoxyl(s), bis(4-*tert*-butylphenyl)-(4-hydrogalvinoxylphenyl)methoxymethane **1ad**, tris(4-hydrogalvinoxylphenyl)methoxymethane **2ad**, and tris{4-[bis(4-hydrogalvinoxylphenyl)methoxymethyl]phenyl}methoxymethane **3ad**, were prepared and oxidized to the corresponding galvinoxyl radicals, **1af**, **2af**, and **3af**, which have one, three, and six galvinoxyl radical(s), respectively. Chemical reduction of the galvinoxyl radicals with a Na/K alloy gave stable intermediates, *i.e.*, the tetraanion, decaanion, and docosaanion. The tetraanion was oxidized with an equimolar amount of iodine at *ca.* 170 K to the galvinoxyl radical-combined triphenylmethyl radical **1cf**. The ESR signal of the biradical at room temperature indicated an exchange interaction between the two radicals. The spectrum at 140 K had a zero-field splitting and  $\Delta M_S = \pm 2$  transition signal at half-field, which are characteristic of a multiplet species. [DOI 10.1295/polymj.37.284]

**KEY WORDS** Dendrimer / Triphenylmethane / Galvinoxyl Radical / High-spin Molecule / Non-Kekulé Structure /

The synthetic research of high-spin molecules and polymers for a purely organic-derived magnetic material has been of current interest in the past two decades.<sup>1–4</sup> High-spin molecules have been synthesized based on the molecular design to satisfy a  $\pi$ -conjugated, but non-Kekulé and non-disjoint connectivity among the multiple radical sites or nonbonding molecular orbitals of the unpaired electrons, which realizes a strong through-bond ferromagnetic exchange interaction.<sup>5–9</sup> Organic radicals with both chemical stability and spin-delocalization are desirable spin sources for the high-spin molecules. *Meta*-connected triphenylmethyl radicals have been extensively studied as such a spin source by one of the coauthors (A.R.). This work eventually led to a highly cross-linked network polymer with a magnetic ordering and a huge magnetic moment corresponding to  $S$  (spin quantum number)  $> 5000$ .<sup>10–13</sup> However, the triarylmethyl radical survives only below 170 K. Chemically stable radicals would facilitate studies of super high-spin molecules for molecular-based magnetic materials.

The galvinoxyl radical formed through the oxidation of 3,3',5,5'-tetra-*tert*-butyl-4,4'-dihydroxydiphenylmethane is a stable phenoxyl-based radical at ambient conditions, and can be isolated as a crystal.<sup>14–16</sup> Its chemical and magnetic properties have been well studied, and it has also been extended to homologous oligomers,<sup>17,18</sup> such as Yang's biradical which is



**Chart 1.**

composed of galvinoxyl residues and a stable triplet biradical.<sup>19</sup>

In this study, we combine a triphenylmethyl radical and a galvinoxyl radical based on the molecular design such that a triphenylmethyl radical is substituted at the *para*-positions with galvinoxyl radicals both to sterically protect the triphenylmethyl radical and to delocalize the spins over the  $\pi$ -conjugated molecule.<sup>20,21</sup> The triphenylmethyl radical combined with a galvinoxyl radical is expected to become a new, stable high-spin molecule. The second aspect of the molecular design is a branched coupling pathway among the radical spins to give a strong spin-exchange interaction in the  $\pi$ -conjugated system. A dendritic extension is applied in this study to synthesize a well and regularly branched  $\pi$ -conjugated structure by satisfying a formal requirement for high-spin ground state, *i.e.*, non-Kekulé and nondisjoint connectivity. A high-

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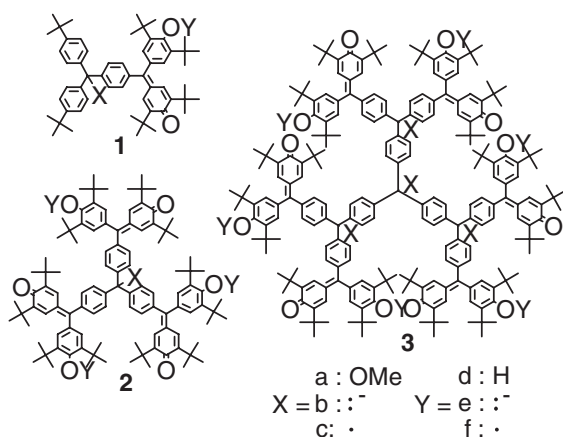
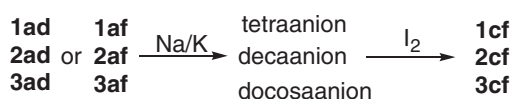


Chart 2.



Scheme 1.

er molecular weight extension may be attained using the same iterative synthetic procedure.<sup>22,23</sup> The dendritic extension is also expected to produce a high solvent-solubility of the polyradical and a chemical stability resulting from the terminal galvinoxyl groups.

In this paper, we report the synthesis of bis(4-*tert*-butylphenyl)-(4-hydroxyphenyl)methoxymethane **1ad**, which is a simple model of the triphenylmethane combined with a hydroxyphenyl group at the *para*-position, and the dendritic extensions, tris(4-hydroxyphenyl)methoxymethane **2ad** and tris[4-{bis(4-hydroxyphenyl)methoxymethyl}phenyl]methoxy methane **3ad**. These compounds, **1ad**, **2ad**, and **3ad**, were reduced to the corresponding tetraanion, decaanion, and docosaanion, respectively, and oxidized to the corresponding radicals, **1cf**, **2cf**, and **3cf**, respectively. The preparation of these radicals and their magnetic properties were also discussed.

## EXPERIMENTAL

### (4-Bromophenyl)-bis(4-*tert*-butylphenyl)methanol.

A 1.6 M hexane solution (52.0 mL) of *n*-butyllithium (81.2 mmol) was slowly added to a 410 mL THF solution of *p*-bromo-*tert*-butylbenzene (17.4 g, 81.8 mmol) at  $-78^\circ\text{C}$  under  $\text{N}_2$ . The solution was warmed to  $0^\circ\text{C}$  and stirred for 30 min. The solution was cooled to  $-78^\circ\text{C}$  again, and methyl *p*-bromobenzoate (8.00 g, 2.23 mmol) was added dropwise. The resulting mixture was stirred for 20 h at  $-78^\circ\text{C}$ , and quenched with aqueous ammonium chloride solution. The resulting mixture was extracted with ether, and the organic layer

was dried over magnesium sulfate. After removal of the solvent, the recrystallization from hexane gave (4-bromophenyl)-bis(4-*tert*-butylphenyl)methanol (8.91 g, Yield 53%) as a white crystal (mp  $181.0\text{--}181.4^\circ\text{C}$ ):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.42 (d,  $J = 8.6$  Hz, 4H, aryl), 7.32 (d,  $J = 8.6$  Hz, 2H, aryl), 7.20 (d,  $J = 8.6$  Hz, 4H, aryl), 7.15 (d,  $J = 8.6$  Hz, 2H, aryl), 2.70 (s, 1H, OH), 1.31 (s, 18H, *t*-Bu);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  150.29, 146.19, 143.53, 130.82, 129.64, 127.45, 124.85, 121.11, 81.36, 34.47, 31.35; (KBr pellet): 3582 ( $\nu_{\text{O-H}}$ ), 2961  $\text{cm}^{-1}$  ( $\nu_{\text{Ar C-H}}$ ); Mass: calcd for M 451.44, found ( $m/z$ ) 451 ( $\text{M}^+$ ).

(4-Bromophenyl)-bis(4-*tert*-butylphenyl)methoxymethane **4**. A 30 mL THF solution of (4-bromophenyl)-bis(4-*tert*-butylphenyl)methanol (4.0 g, 8.86 mmol) was slowly added to the 300 mL THF suspension of sodium hydride (1.10 g, 44.3 mmol) and stirred at  $0^\circ\text{C}$  for 1 h. Iodomethane (8.80 mL, 142 mmol) was added, and the reaction mixture was allowed to warm to room temperature and stirred overnight. The mixture was quenched with water. The resulting mixture was extracted with ether, and the organic layer was dried over magnesium sulfate. After removal of the solvent, the recrystallization from methanol gave (4-bromophenyl)-bis(4-*tert*-butylphenyl)methoxymethane **4** (3.75 g, Yield 91%) as a white crystal (mp  $171.3\text{--}172.6^\circ\text{C}$ ):  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 (d,  $J = 8.9$  Hz, 2H, aryl), 7.34 (d,  $J = 8.9$  Hz, 2H, aryl), 7.30–7.29 (m, 8H, aryl), 3.03 (s, 3H, methoxy), 1.30 (s, 18H, *t*-Bu);  $^{13}\text{C}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  149.85, 144.44, 140.06, 130.73, 130.15, 128.45, 124.68, 120.64, 86.39, 52.02, 34.41, 31.35; IR (KBr pellet): 2957 ( $\nu_{\text{Ar C-H}}$ ), 1267  $\text{cm}^{-1}$  ( $\nu_{\text{C-O-C}}$ ); Mass: calcd for M 465.47, found ( $m/z$ ) 465 ( $\text{M}^+$ ).

Bis(4-*tert*-butylphenyl)-(4-formylphenyl)methoxymethane. A 1.6 M hexane solution (4.00 mL) of *n*-butyllithium (6.45 mmol) was slowly added to a 65 mL THF solution of (4-bromophenyl)-bis(4-*tert*-butylphenyl)methoxymethane **4** (3.00 g, 6.45 mmol) at  $-78^\circ\text{C}$  under  $\text{N}_2$ . The solution was warmed to  $0^\circ\text{C}$  and stirred for 30 min. Dimethylformamide (1.5 mL, 9.68 mmol) was added slowly, and the reaction mixture was stirred for 20 h at room temperature. The mixture was quenched with aqueous ammonium chloride solution. The resulting mixture was extracted with ether, and the organic layer was dried over magnesium sulfate. After removal of the solvent, the purification by chromatography with a silica gel column and a chloroform eluent gave bis(4-*tert*-butylphenyl)-(4-formylphenyl)methoxymethane (2.20 g, Yield 35%) as a white powder:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  9.97 (s, 1H, formyl), 7.80 (d,  $J = 8.2$  Hz, 2H, aryl), 7.68 (d,  $J = 8.2$  Hz, 2H, aryl), 7.33–7.29 (m, 8H, aryl), 3.05 (s, 3H, methoxy), 1.31 (s, 18H, *t*-Bu);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  192.01, 152.79, 150.16, 139.38, 134.71,

129.25, 128.76, 128.39, 86.70, 52.079, 34.46, 31.35; (KBr pellet): 2962 ( $\nu_{\text{Ar C-H}}$ ), 1728  $\text{cm}^{-1}$  ( $\nu_{\text{C=O}}$ ); Mass: calcd for M 476.18, found ( $m/z$ ) 476 ( $\text{M}^+$ ).

*Bis(4-tert-butylphenyl)-(4-methoxycarbonylphenyl)-methoxymethane 5.* Amidosulfuric acid (500 mg, 4.82 mmol) and sodium chlorite (400 mg, 4.82 mmol) were added to a 16 mL acetone and 10 mL chloroform solution of bis(4-tert-butylphenyl)-(4-formylphenyl)-methoxymethane (200 mg, 0.48 mmol). The reaction mixture was stirred at room temperature for 18 h. Five milliliters of 2 N HCl was added and the resulting mixture was stirred for 1 h. After removal of the solvent, the crude product was filtrated and washed with water to give tris(4-carboxyphenyl)methoxymethane as a white powder. The powder was dissolved in the 500 mL methanol containing sulfuric acid (50 mL). The mixture was stirred and refluxed for 12 h, and neutralize with sodium carbonate. The resulting mixture was extracted with chloroform, and the organic layer was dried over magnesium sulfate. After removal of the solvent, the purification by chromatography with a silica gel column and a chloroform eluent gave bis(4-tert-butylphenyl)-(4-methoxycarbonylphenyl)-methoxymethane **5** as a white powder (100 mg, Yield 47%);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (d,  $J = 8.9$  Hz, 2H, aryl), 7.57 (d,  $J = 8.9$  Hz, 2H, aryl), 7.33–7.25 (m, 8H, aryl), 3.87 (s, 3H, methylester), 3.04 (s, 3H, methoxy), 1.31 (s, 18H, *t*-Bu);  $^{13}\text{C}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  167.00, 150.71, 149.97, 139.76, 129.03, 128.69, 128.33, 128.07, 124.67, 86.65, 52.04, 34.42, 31.31; IR (KBr pellet): 2960 ( $\nu_{\text{Ar C-H}}$ ), 1724  $\text{cm}^{-1}$  ( $\nu_{\text{C=O}}$ ); Mass: calcd for M 444.61, found ( $m/z$ ) 444 ( $\text{M}^+$ ).

*Bis(4-tert-butylphenyl)-(4-hydrogalvinoxylphenyl)-methoxymethane 1ad.* A 1.6 M hexane solution (1.2 mL) of *n*-butyllithium (2.00 mmol) was slowly added to a 25 mL THF solution of (4-bromo-2,6-di-*tert*-butylphenoxy)trimethylsilane (5.00 g, 14.0 mmol) at  $-78^\circ\text{C}$  under  $\text{N}_2$ . The solution was warmed to  $0^\circ\text{C}$  and stirred for 30 min. The solution was cooled to  $-78^\circ\text{C}$  again, and a 5 mL THF solution of tris(4-methoxycarbonylphenyl)methoxymethane **5** (100 mg, 0.23 mmol) was added slowly. The resulting mixture was stirred for 20 h at  $-78^\circ\text{C}$ , and quenched with aqueous ammonium chloride solution. The resulting mixture was extracted with ether, and the organic layer was dried over magnesium sulfate. Evaporation gave a red oil. Five milliliters of 10 N HCl was added to a 50 mL methanol and 50 mL THF solution of the red oil, and the mixture was stirred at room temperature for 1 h. The resulting mixture was extracted with chloroform, and the organic layer was dried over magnesium sulfate. After removal of the solvent, the purification by chromatography with a silica gel column and a hexane/ethyl acetate = 10/1 eluent gave bis(4-

*tert*-butylphenyl)-(4-hydrogalvinoxylphenyl)methoxymethane **1ad** as a red powder (96 mg, Yield 53%);  $^1\text{H}$  NMR (THF- $d_8$ , 500 MHz)  $\delta$  7.49 (d,  $J = 8.5$  Hz, 2H, aryl), 7.36–7.31 (m, 8H, aryl), 7.26 (d,  $J = 2.5$  Hz, 1H, quinone), 7.18 (d,  $J = 8.5$  Hz, 2H, aryl), 7.08 (d,  $J = 2.5$  Hz, 1H, quinone), 7.01 (s, 2H, phenoxy), 5.48 (s, 1H, phenol), 3.12 (s, 3H, methoxy), 1.39 (s, 18H, *t*-Bu), 1.32 (s, 18H, *t*-Bu), 1.29 (s, 9H, *t*-Bu), 1.22 (s, 9H, *t*-Bu);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  186.1, 158.0, 155.4, 149.8, 146.7, 146.4, 146.1, 140.2, 139.7, 135.2, 132.7, 132.4, 131.8, 131.5, 130.0, 128.6, 128.5, 127.9, 124.6, 86.8, 52.1, 35.3, 35.2, 34.4, 34.3, 31.3, 30.3, 29.7, 29.4; IR (KBr pellet): 3585 ( $\nu_{\text{O-H}}$ ), 2957 ( $\nu_{\text{Ar C-H}}$ ), 1602 ( $\nu_{\text{C=O}}$ ), 1245  $\text{cm}^{-1}$  ( $\nu_{\text{C-O-C}}$ ); Mass: calcd for M 807.2, found ( $m/z$ ) 807.6 ( $\text{M}^+$ ).

*Tris[4-(1,3-dioxolan-2-yl)phenyl]methanol.* A 1.6 M hexane solution (26.0 mL) of *n*-butyllithium (41.1 mmol) was slowly added to a 450 mL THF solution of 2-(4-bromophenyl)-1,3-dioxolane (10.0 g, 43.9 mmol) at  $-78^\circ\text{C}$  under  $\text{N}_2$ . The solution was warmed to  $0^\circ\text{C}$  and stirred for 1 h. The solution was cooled to  $-78^\circ\text{C}$  again, and dimethyl carbonate (1.28 g, 13.3 mmol) was added dropwise. The resulting mixture was stirred for 20 h at  $-78^\circ\text{C}$ , and quenched with aqueous ammonium chloride solution. The resulting mixture was extracted with ether, and the organic layer was dried over magnesium sulfate. After removal of the solvent, the purification by chromatography with a silica gel column and a chloroform/hexane/methanol = 20/10/1 eluent and the recrystallization from hexane gave tris[4-(1,3-dioxolane-2-yl)phenyl]methanol (2.20 g, Yield 35%) as a colorless crystal (mp  $187.2$ – $188.7^\circ\text{C}$ ):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.40 (d,  $J = 8.0$  Hz, 6H, aryl), 7.28 (d,  $J = 8.0$  Hz, 6H, aryl), 5.78 (s, 3H, dioxolane), 4.16–4.02 (m, 12H, dioxolane), 2.95 (s, 1H, OH);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  147.54, 136.90, 127.96, 126.07, 103.34, 81.58, 65.30; IR (KBr pellet): 3392 ( $\nu_{\text{O-H}}$ ), 2888  $\text{cm}^{-1}$  ( $\nu_{\text{Ar C-H}}$ ); Mass: calcd for M 476.52, found ( $m/z$ ) 476 ( $\text{M}^+$ ).

*Tris[4-(1,3-dioxolan-2-yl)phenyl]methoxymethane 6.* A 30 mL THF solution of tris(4-(1,3-dioxolane-2-yl)phenyl)methanol (800 mg, 1.68 mmol) was slowly added to a 140 mL THF suspension of sodium hydride (336 mg, 8.40 mmol) and stirred at  $0^\circ\text{C}$  for 1 h. Iodomethane (1.68 mL, 26.9 mmol) was added slowly, and the reaction mixture was allowed to warm to room temperature and stirred overnight. The mixture was quenched with water. The resulting mixture was extracted with ether, and the organic layer was dried over magnesium sulfate. After removal of solvent, the recrystallized with hexane gave tris[4-(1,3-dioxolane-2-yl)phenyl]methoxymethane **6** (608 mg, Yield 74%) as a colorless crystal:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 (d,  $J = 6.6$  Hz, 6H, aryl), 7.40 (d,  $J =$

6.6 Hz, 6H, aryl), 5.78 (s, 3H, dioxolane), 4.15–4.02 (m, 12H, dioxolane), 3.03 (s, 3H, methoxy);  $^{13}\text{C}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  144.71, 136.56, 128.78, 125.93, 103.50, 86.72, 65.32, 52.09; IR (KBr pellet): 2831 ( $\nu_{\text{Ar C-H}}$ ), 1210  $\text{cm}^{-1}$  ( $\nu_{\text{C-O-C}}$ ); Mass: calcd for M 490.54, found ( $m/z$ ) 491 ( $\text{M}^+$ ).

*Tris(4-formylphenyl)methoxymethane.* *p*-Toluene-sulfonic acid monohydrate (0.30 g, 1.58 mmol) and water (2.5 mL) were added to a 70 mL acetone solution of tris(4-(1,3-dioxolane-2-yl-phenyl)methoxymethane **6** (1.00 g, 2.10 mmol), and the mixture was refluxed for 3 h. The resulting mixture was extracted with chloroform, and the organic layer was dried over magnesium sulfate. After removal of the solvent, the purification by chromatography with a silica gel column and a chloroform eluent gave tris(4-formylphenyl)methoxymethane as a colorless oil (0.67 g, Yield 90%);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.95 (s, 3H, formyl), 7.82 (d,  $J = 8.6$  Hz, 6H, aryl), 7.58 (d,  $J = 8.6$  Hz, 6H, aryl), 3.06 (s, 3H, methoxy);  $^{13}\text{C}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  191.55, 148.91, 135.66, 129.61, 129.17, 86.89, 52.53; IR (KBr pellet): 2888 ( $\nu_{\text{Ar C-H}}$ ), 1702  $\text{cm}^{-1}$  ( $\nu_{\text{C=O}}$ ); Mass: calcd for M 358.39, found ( $m/z$ ) 358 ( $\text{M}^+$ ).

*Tris(4-methoxycarbonylphenyl)methoxymethane 7.* Amidosulfuric acid (6.50 g, 67.1 mmol) and sodium chlorite (6.00 g, 67.0 mmol) were added to a 220 mL acetone and 130 mL chloroform solution of tris(4-formylphenyl)methoxymethane (0.80 g, 2.23 mmol). The reaction mixture was stirred at room temperature for 18 h. 50 mL of 2 N HCl was added and the resulting mixture was stirred for 1 h. After removal of the solvent, the crude product was filtrated and washed with water to give tris(4-carboxyphenyl)methoxymethane as a white powder. The powder was dissolved in the 500 mL methanol containing sulfuric acid (50 mL) were dissolved in 500 mL methanol. The mixture was stirred and refluxed for 12 h, and neutralized with sodium carbonate. The resulting mixture was extracted with chloroform, and the organic layer was dried over magnesium sulfate. After removal of the solvent, the purification by chromatography with a silica gel column and a hexane/ethyl acetate = 2/1 eluent gave tris(4-methoxycarbonylphenyl)methoxymethane **7** as an oil (558 mg, Yield 56%);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 (d,  $J = 8.6$  Hz, 6H, aryl), 7.49 (d,  $J = 8.6$  Hz, 6H, aryl), 3.91 (s, 9H, methylester), 3.08 (s, 3H, methoxy);  $^{13}\text{C}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  140.85, 136.52, 129.21, 123.58, 102.21, 95.18, 65.45; IR (KBr pellet): 2951 ( $\nu_{\text{Ar C-H}}$ ), 1724  $\text{cm}^{-1}$  ( $\nu_{\text{C=O}}$ ); Mass: calcd for M 448.46, found ( $m/z$ ) 448 ( $\text{M}^+$ ).

*Tris(4-hydrogalvinoxylphenyl)methoxymethane 2ad.* A 1.6 M hexane solution (7.0 mL) of *n*-butyllithium (12.0 mmol) was slowly added to a 140 mL THF solution of (4-bromo-2,6-di-*tert*-butylphenoxy)trimethyl-

silane (5.00 g, 14.0 mmol) at  $-78^\circ\text{C}$  under  $\text{N}_2$ . The solution was warmed to  $0^\circ\text{C}$  and stirred for 1 h. The solution was cooled to  $-78^\circ\text{C}$  again, and a 10 mL THF solution of tris(4-methoxycarbonylphenyl)methoxymethane (100 mg, 0.223 mmol) was added slowly. The resulting mixture was stirred for 20 h at  $-78^\circ\text{C}$ , and quenched with aqueous ammonium chloride solution. The resulting mixture was extracted with ether, and the organic layer was dried over magnesium sulfate. Evaporation gave a red oil. Ten milliliters of 10 N HCl was added to a 50 mL methanol and 100 mL THF solution of the red oil. The mixture was stirred at room temperature for 1 h. The resulting mixture was extracted with chloroform, and the organic layer was dried over magnesium sulfate. After removal of the solvent, the purification by chromatography with a silica gel column and a hexane/ethyl acetate = 4/1 eluent gave tris(4-mhydrogalvinoxylphenyl)methoxymethane **2ad** as a red powder (334 mg, Yield 97%);  $^1\text{H}$  NMR (THF- $d_8$ , 500 MHz)  $\delta$  7.59 (d,  $J = 8.5$  Hz, 6H, aryl), 7.35 (d,  $J = 2.1$  Hz, 3H, quinone), 7.29 (d,  $J = 8.5$  Hz, 6H, aryl), 7.15 (d,  $J = 2.1$  Hz, 3H, quinone), 6.73 (s, 6H, phenoxy), 5.50 (s, 3H, phenol), 3.20 (s, 3H, methoxy), 1.40 (s, 54H, *t*-Bu), 1.29 (s, 27H, *t*-Bu), 1.21 (s, 27H, *t*-Bu);  $^{13}\text{C}$  NMR (THF- $d_8$ , 500 MHz)  $\delta$  186.1, 157.2, 155.5, 147.0, 146.6, 144.1, 140.5, 135.3, 132.4, 131.8, 131.7, 129.9, 128.9, 128.0, 86.9, 52.3, 35.3, 35.2, 34.4, 30.3, 29.7, 29.5; IR (KBr pellet): 3633 ( $\nu_{\text{O-H}}$ ), 2956 ( $\nu_{\text{Ar C-H}}$ ), 1600 ( $\nu_{\text{C=O}}$ ), 1239  $\text{cm}^{-1}$  ( $\nu_{\text{C-O-C}}$ ); Mass: calcd for M 1536, found ( $m/z$ ) 1537 ( $\text{M}^+$ ).

*(4-Bromophenyl)-bis[4-(1,3-dioxolane-2-yl)phenyl]methanol.* A 1.59 M hexane solution (79.0 mL) of *n*-butyllithium (0.126 mol) was slowly added to a 480 mL THF solution of 2-(4-bromophenyl)-1,3-dioxolane (30.0 g, 0.131 mol) at  $-78^\circ\text{C}$  under  $\text{N}_2$ , and the mixture was stirred for 30 min. Methyl *p*-bromobenzoate (12.8 g, 0.595 mol) was added dropwise, and the solution was warmed to room temperature. The resulting mixture was stirred for 20 h, and quenched with aqueous ammonium chloride solution. The resulting mixture was extracted with ether, and the organic layer was dried over magnesium sulfate. After removal of the solvent, the purification by chromatography with a silica gel column and a chloroform eluent gave (4-bromophenyl)-bis[4-(1,3-dioxolane-2-yl)phenyl]methanol (29.2 g, Yield 99%) as a colorless oil:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.41–7.39 (m, 6H, aryl), 7.25 (d,  $J = 8.2$  Hz, 4H, aryl), 7.14 (d,  $J = 8.8$  Hz, 2H, aryl), 5.78 (s, 2H, dioxolane), 4.13–4.00 (m, 8H, dioxolane), 2.889 (s, 1H, OH);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  147.2, 145.6, 137.1, 131.0, 129.7, 127.9, 126.2, 121.5, 103.4, 81.4, 65.3; Mass: calcd for M 483.3, found ( $m/z$ ) 483 ( $\text{M}^+$ ).

*(4-Bromophenyl)-bis[4-(1,3-dioxolane-2-yl)phenyl]-*

**methoxymethane 8.** A 50 mL THF solution of (4-bromophenyl)-bis[4-(1,3-dioxolane-2-yl)phenyl]methanol (29.0 g, 60.0 mmol) was slowly added to a 450 mL THF suspension of sodium hydride (14.4 g, 0.600 mol) and stirred at 0 °C for 3 h. Iodomethane (22.4 mL, 0.359 mmol) was added slowly, and the reaction mixture was allowed to warm to room temperature and stirred overnight. The mixture was quenched with water. The resulting mixture was extracted with ether, and the organic layer was dried over magnesium sulfate. After removal of the solvent, the purification by chromatography with a silica gel column and a dichloromethane/methanol = 30/1 eluent gave (4-bromophenyl)-bis[4-(1,3-dioxolane-2-yl)phenyl]methoxymethane **8** (19.5 g, Yield 65%) as a colorless crystal: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.41–7.26 (m, 12H, aryl), 5.782 (s, 2H, dioxolane) 4.14–4.01 (m, 8H, dioxolane), 3.03 (s, 3H, methoxy); <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>) δ 144.2, 143.2, 136.8, 130.9, 130.3, 128.7, 126.1, 121.2, 103.5, 86.5, 65.4, 52.1; Mass: calcd for M 497.4, found (*m/z*) 497 (M<sup>+</sup>).

**Tris(4-{bis[4-(1,3-dioxolane-2-yl)phenyl]methoxymethyl}phenyl)methanol.** A 1.56 M hexane solution (18.0 mL) of *n*-butyllithium (28.1 mmol) was slowly added to a 180 mL THF solution of (4-bromophenyl)-bis[4-(1,3-dioxolane-2-yl)phenyl]methoxymethane **8** (14.2 g, 28.6 mmol) at –78 °C under N<sub>2</sub>. Dimethyl carbonate (780 mg, 8.66 mmol) was added dropwise, and the solution was warmed to room temperature. The resulting mixture was stirred for 20 h at room temperature, and quenched with aqueous ammonium chloride solution. The resulting mixture was extracted with ether, and the organic layer was dried over magnesium sulfate. After removal of the solvent, the purification by chromatography with a silica gel column and a dichloromethane/methanol = 30/1 eluent gave tris(4-{bis[4-(1,3-dioxolane-2-yl)phenyl]methoxymethyl}phenyl)methanol (9.80 g, Yield 87%) as a yellow powder: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 7.44 (d, *J* = 8.5 Hz, 12H, aryl), 7.40 (d, *J* = 8.5 Hz, 12H, aryl), 7.32 (d, *J* = 8.8 Hz, 6H, aryl), 7.13 (d, *J* = 8.8 Hz, 6H, aryl), 5.78 (s, 6H, dioxolane), 4.13–4.01 (m, 24H, dioxolane), 3.02 (s, 9H, methoxy), 2.789 (s, 1H, OH); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 500 MHz) δ 1145.3, 144.8, 142.5, 136.4, 128.8, 128.3, 127.4, 125.9, 103.5, 86.7, 81.5, 65.3, 52.1; FAB Mass: calcd for M 1281.4, found (*m/z*) 1281 (M<sup>+</sup>).

**Tris(4-{bis[4-(1,3-dioxolane-2-yl)phenyl]methoxymethyl}phenyl)methoxymethane 9.** A 5 mL THF solution of tris(4-{bis[4-(1,3-dioxolane-2-yl)phenyl]methoxymethyl}phenyl)methanol (300 mg, 0.234 mmol) was slowly added to 12 mL THF suspension of sodium hydride (1.44 g, 60 mmol) and stirred at 0 °C for 3 h. Iodomethane (0.219 mL, 3.52 mmol) was added slowly, and the reaction mixture was allowed to

warm to room temperature and stirred overnight. The mixture was quenched with water. The resulting mixture was extracted with ether, and the organic layer was dried over magnesium sulfate. After removal of the solvent, the purification by chromatography with a silica gel column and a dichloromethane/methanol = 30/1 eluent gave tris(4-{bis[4-(1,3-dioxolane-2-yl)phenyl]methoxymethyl}phenyl)methoxymethane **9** (297 mg, Yield 98%) as a white powder: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.44 (d, *J* = 8.5 Hz, 12H, aryl), 7.40 (d, *J* = 8.2 Hz, 12H, aryl), 7.301 (d, *J* = 8.8 Hz, 6H, aryl), 7.27 (d, *J* = 8.5 Hz, 6H, aryl), 5.780 (s, 6H, dioxolane), 4.14–3.99 (m, 24H, dioxolane), 3.01 (s, 9H, methoxy), 3.00 (s, 3H, methoxy); <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>) δ 144.8, 142.3, 142.0, 136.4, 128.7, 128.2, 128.1, 125.9, 103.6, 86.7, 86.6, 65.3, 52.2, 52.1; FAB Mass: calcd for M 1295.5, found (*m/z*) 1295 (M<sup>+</sup>).

**Tris(4-[bis(4-formylphenyl)methoxymethyl]phenyl)methoxymethane.** *p*-Toluenesulfonic acid monohydrate (350 mg, 1.84 mmol) and water (6.2 mL) were added to a 84 mL acetone solution of tris(4-{bis[4-(1,3-dioxolane-2-yl)phenyl]methoxymethyl}phenyl)methoxymethane **9** (900 mg, 0.695 mmol), and the mixture was refluxed for 48 h. The resulting mixture was extracted with chloroform, and the organic layer was dried over magnesium sulfate. After removal of the solvent, the purification by chromatography with a silica gel column and a chloroform eluent gave tris(4-[bis(4-formylphenyl)methoxymethyl]phenyl)methoxymethane as a colorless oil (595 mg, Yield 83%); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.99 (s, 6H, formyl), 7.83 (d, *J* = 8.3 Hz, 12H, aryl), 7.63 (d, *J* = 8.3 Hz, 12H, aryl), 7.39 (d, *J* = 8.5 Hz, 6H, aryl), 7.31 (d, *J* = 8.8 Hz, 6H, aryl), 3.053 (s, 9H, methoxy), 3.043 (s, 3H, methoxy); <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>) δ 191.6, 149.9, 142.9, 140.4, 135.3, 129.4, 128.9, 128.6, 128.5, 86.7, 86.4, 52.3, 52.2; FAB Mass: calcd for M 1031.1, found (*m/z*) 1031 (M<sup>+</sup>).

**Tris(4-[bis(4-methoxycarbonylphenyl)methoxymethyl]phenyl)methoxymethane 10.** Amidosulfuric acid (120 mg, 1.24 mmol) and sodium chlorite (100 mg, 1.11 mmol) were added to a 15 mL acetone and 5 mL chloroform solution of tris(4-[bis(4-formylphenyl)methoxymethyl]phenyl)methoxymethane (71.0 mg, 6.89 × 10<sup>-2</sup> mmol). The reaction mixture was stirred at room temperature for 18 h. Seven and half milliliters of 2 N HCl was added and the resulting mixture was stirred for 1 h. After removal of the solvent, the crude product was filtrated and washed with water to give tris(4-[bis(4-carboxyphenyl)methoxymethyl]phenyl)methoxymethane as a white powder. The powder was dissolved in the 10 mL methanol containing sulfuric acid (1 mL) were dissolved. The mixture was stirred at room temperature for 12 h, and neutral-

ized with sodium carbonate. The resulting mixture was extracted with chloroform, and the organic layer was dried over magnesium sulfate. After removal of the solvent, the purification by chromatography with a silica gel column and a hexane/ethyl acetate = 1/1 eluent gave tris{4-[bis(4-methoxycarbonylphenyl)methoxymethyl]phenyl}methoxymethane **10** as a white powder (68 mg,  $5.61 \times 10^{-2}$  mmol, Yield 81%);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (d,  $J = 8.2$  Hz, 12H, aryl), 7.51 (d,  $J = 8.3$  Hz, 12H, aryl), 7.34 (d,  $J = 8.8$  Hz, 6H, aryl), 7.29 (d,  $J = 8.5$  Hz, 6H, aryl), 3.89 (s, 18H, methylester), 3.03 (s, 9H, methoxy), 3.018 (s, 3H, methoxy);  $^{13}\text{C}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  166.7, 148.7, 142.8, 140.9, 129.2, 129.0, 128.4, 128.4, 86.7, 86.5, 52.3, 52.2, 52.1; FAB Mass: calcd for M 1211.3, found ( $m/z$ ) 1211 ( $\text{M}^+$ ).

*Tris[4-{bis(4-hydrogalvinoxylphenyl)methoxymethyl}phenyl]methoxymethane 3ad.* A 1.56 M hexane solution (4.60 mL) of *n*-butyllithium (7.18 mmol) was slowly added to a 80 mL THF solution of (4-bromo-2,6-di-*tert*-butylphenoxy)trimethylsilane (2.80 g, 0.797 mmol) at  $-78^\circ\text{C}$  under  $\text{N}_2$ . A 1 mL THF solution of tris{4-[bis(4-methoxycarbonylphenyl)methoxymethyl]phenyl}methoxymethane **10** (64 mg,  $5.28 \times 10^{-2}$  mmol) was added slowly, and the solution was allowed to warm to room temperature. The mixture was stirred for 20 h at  $-78^\circ\text{C}$ , and quenched with aqueous ammonium chloride solution. The resulting mixture was extracted with ether, and the organic layer was dried over magnesium sulfate. Evaporation gave a yellow powder. The powder was dissolved to the mixture of 3 mL methanol and 4 mL THF, and 0.5 mL of 10 N HCl was added. The mixture was stirred at room temperature for 5 min. The resulting mixture was extracted with chloroform, and the organic layer was dried over magnesium sulfate. After removal of the solvent, the purification by chromatography with a silica gel column and a hexane/ethyl acetate = 4/1 eluent gave tris[4-{bis(4-hydrogalvinoxylphenyl)methoxymethyl}phenyl]methoxymethane **3ad** as a yellow powder (95 mg,  $2.28 \times 10^{-2}$  mmol, Yield 53%);  $^1\text{H}$  NMR (THF- $d_8$ , 500 MHz)  $\delta$  7.56 (d,  $J = 8.5$  Hz, 12H, aryl), 7.47 (d,  $J = 8.8$  Hz, 6H, aryl), 7.44 (d,  $J = 8.8$  Hz, 6H, aryl), 7.34 (d,  $J = 2.4$  Hz, 6H, quinone), 7.25 (d,  $J = 8.2$  Hz, 12H, aryl), 7.11 (d,  $J = 2.4$  Hz, 6H, quinone), 7.09 (s, 12H, phenoxy), 6.70 (s, 6H, phenol), 3.13 (s, 9H, methoxy), 2.98 (s, 3H, methoxy), 1.38 (s, 108H, *t*-Bu), 1.28 (s, 54H, *t*-Bu), 1.18 (s, 54H, *t*-Bu);  $^{13}\text{C}$  NMR (THF- $d_8$ , 500 MHz)  $\delta$  186.1, 158.2, 156.9, 147.5, 147.0, 145.8, 143.8, 143.1, 141.6, 137.5, 133.1, 132.9, 132.4, 130.6, 129.5, 129.3, 129.1, 129.0, 87.7, 87.4, 52.5, 52.4, 36.0, 35.9, 35.3, 30.6, 30.5, 30.1; MALDI-TOF Mass: calcd for M 3386.8, found ( $m/z$ ) 3388 ( $\text{M}^+$ ).

*Other Materials.* All solvents were purified by dis-

tillation just before the usage. Tetrabutylammonium tetrafluoroborate and potassium ferricyanide were purified by recrystallization. All other reagents were used as received.

#### Preparation of the Galvinoxyl Radicals

Aqueous solutions of excess sodium hydroxide and of potassium ferricyanide were successively added to a 2.5 mM toluene solution of the hydroxyl precursor, **1ad**, **2ad**, and **3ad**, and the mixture was vigorously stirred at room temperature. Color of the organic layer changed from blue to deep brown. After stirring for 30 min, the organic layer was extracted with toluene. The extract was washed with water, dried over anhydrous sodium sulfate, and evaporated to give brownish powder of the galvinoxyl radical, **1af**, **2af**, and **3af**.

#### Anionization

Five milligrams of galvinoxyl radical, **1af**, **2af**, or **3af**, or of the hydrogalvinoxyl **1ad** was placed in a Schlenk tube equipped with a high-vacuum PTFE stopcock, and then dried under vacuum for 1 d. THF (0.3 mL) was vacuum transferred to the Schlenk tube, and a drop of Na/K alloy was added under an Ar gas flow. After the reaction mixture was stirred for 24 h at room temperature, the anion was quenched by addition of excess methanol or  $\text{CH}_3\text{OD}$  (99.5%). The resulting mixture was extracted with ether, and the extract was washed with water, dried, and evaporated. The resultant deuterated or hydrated triphenylmethanes were examined by  $^1\text{H}$  NMR spectroscopy.

*Anionized and Hydrated Bis(4-*tert*-butylphenyl)-(4-hydrogalvinoxylphenyl)methoxymethane 1ad.*  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 7.25 (d,  $J = 6.4$  Hz, 4H, aryl), 7.02 (d,  $J = 8.9$  Hz, 4H, aryl), 7.01 (s, 4H, aryl), 6.91 (s, 4H, phenol aryl), 5.43 (s, 1H,  $\text{Ph}_3\text{C}-\underline{\text{H}}$ ), 5.28 (s, 1H,  $\text{Ph}_3\text{C}-\underline{\text{H}}$ ), 5.01 (s, 2H, phenol), 1.36 (s, 36H, *t*-Bu), 1.29 (s, 18H, *t*-Bu); IR (KBr pellet): 3645 ( $\nu_{\text{O-H}}$ ), 2957 ( $\nu_{\text{Ar C-H}}$ ), 1434  $\text{cm}^{-1}$  ( $\delta_{\text{C-H}}$ ); FAB-Mass: calcd for M 778.5, found ( $m/z$ ) 778.6 ( $\text{M}^+$ ).

*Anionized and Deuterated Bis(4-*tert*-butylphenyl)-(4-hydrogalvinoxylphenyl)methoxymethane 1ad.*  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 7.26 (d,  $J = 8.2$  Hz, 4H, aryl), 7.02 (d,  $J = 9.4$  Hz, 4H, aryl), 7.01 (s, 4H, aryl), 6.90 (s, 4H, phenol aryl), 5.28 (s, 0.9H,  $\text{Ph}_3\text{C}-\underline{\text{H}}$ ), 5.02 (s, 2H, phenol), 1.36 (s, 36H, *t*-Bu), 1.29 (s, 18H, *t*-Bu); IR (KBr pellet): 3643 ( $\nu_{\text{O-H}}$ ), 2957 ( $\nu_{\text{Ar C-H}}$ ), 1434  $\text{cm}^{-1}$  ( $\delta_{\text{C-H}}$ ).

*Anionized and Deuterated Bis(4-*tert*-butylphenyl)-(4-galvinoxylphenyl)methoxymethane 1af.*  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 7.26 (d,  $J = 8.4$  Hz, 4H, aryl), 7.02 (d,  $J = 8.7$  Hz, 4H, aryl), 7.01 (s, 4H, aryl), 6.91 (s, 4H, phenol aryl), 5.44 (s, 0.03H,  $\text{Ph}_3\text{C}-\underline{\text{H}}$ ), 5.29 (s, 0.07H,  $\text{Ph}_3\text{C}-\underline{\text{H}}$ ), 5.01 (s, 2H, phenol), 1.36 (s, 36H, *t*-Bu), 1.29 (s, 18H, *t*-Bu).

Anionized and Hydrated Tris(4-hydroxylphenyl)methoxymethane **2ad**.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 6.96 (d, 6H, aryl), 6.91 (d, 6H, aryl), 6.89 (s, 12H, phenol aryl), 5.47 (s, 1H,  $\text{Ph}_3\text{C-H}$ ), 5.27 (s, 3H,  $\text{Ph}_3\text{C-H}$ ), 5.01 (s, 6H, phenol), 1.34 (s, 108H, *t*-Bu); IR (KBr pellet): 3648 ( $\nu_{\text{O-H}}$ ), 2956 ( $\nu_{\text{Ar C-H}}$ ), 1437  $\text{cm}^{-1}$  ( $\delta_{\text{C-H}}$ );

Anionized and Deuterated Tris(4-galvinoxylphenyl)methoxymethane **2af**.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 6.96 (d, 6H, aryl), 6.91 (d, 6H, aryl), 6.89 (s, 12H, phenol aryl), 5.27 (s, 0.3H,  $\text{Ph}_3\text{C-H}$ ), 5.01 (s, 6H, phenol), 1.34 (s, 108H, *t*-Bu); IR (KBr pellet): 3642 ( $\nu_{\text{O-H}}$ ), 2919 ( $\nu_{\text{Ar C-H}}$ ), 1264  $\text{cm}^{-1}$  ( $\delta_{\text{C-D}}$ ); FAB-Mass: calcd for M 1515.1, found ( $m/z$ ) 1515.2 ( $\text{M}^+$ ).

Anionized and Hydrated Tris[4-{bis(4-hydroxylphenyl)methoxymethyl}phenyl]methoxymethane **3ad**.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 6.97 (d,  $J = 8.5$  Hz, 12H, aryl), 6.93 (d,  $J = 10$  Hz, 12H, aryl), 6.93 (s, 12H, aryl), 6.88 (s, 12H, phenol aryl), 6.87 (s, 12H, phenol aryl), 5.42 (s, 3H,  $\text{Ph}_3\text{C-H}$ ), 5.36 (s, 1H,  $\text{Ph}_3\text{C-H}$ ), 5.26 (s, 6H,  $\text{Ph}_3\text{C-H}$ ), 5.01 (s, 6H, phenol), 5.00 (s, 6H, phenol), 1.34 (s, 108H, *t*-Bu), 1.33 (s, 108H, *t*-Bu); IR (KBr pellet): 3644 ( $\nu_{\text{O-H}}$ ), 2955 ( $\nu_{\text{Ar C-H}}$ ), 1232  $\text{cm}^{-1}$  ( $\delta_{\text{C-D}}$ );

Anionized and Deuterated Tris[4-{bis(4-galvinoxylphenyl)methoxymethyl}phenyl]methoxymethane **3af**.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 6.96 (d,  $J = 8.4$  Hz, 12H, aryl), 6.93 (d,  $J = 6.2$  Hz, 12H, aryl), 6.93 (s, 12H, aryl), 6.88 (s, 12H, phenol aryl), 6.87 (s, 12H, phenol aryl), 5.26 (s, 1H,  $\text{Ph}_3\text{C-H}$ ), 5.01 (s, 6H, phenol), 5.00 (s, 6H, phenol), 1.334 (s, 108H, *t*-Bu), 1.330 (s, 108H, *t*-Bu).

#### Oxidation

Bis(4-*tert*-butylphenyl)-(4-galvinoxylphenyl)methoxymethane **1af** (1.20 mg, 1.49  $\mu\text{mol}$ ) was placed in a quartz reaction vessel equipped with two high-vacuum PTFE stopcocks.<sup>13</sup> The vessel was dried overnight under vacuum at 200 °C using a heating tape except a part containing the galvinoxyl radical **1af**. The vessel was transferred to a glovebox, and a small drop of Na/K alloy was added. Following attachment of the vessel to a vacuum line, Na/K was allowed to come in contact with the galvinoxyl radical, and THF- $d_8$  (0.2–0.3 mL, 99.95% D) was immediately vacuum-transferred from the vessel of the THF- $d_8$  with sodium/benzophenone. After 1 d of stirring at 10 °C, the reaction mixture was filtered under temperature gradient into the quartz tube. An anhydrous THF (5.44  $\mu\text{mol}$ , 25  $\mu\text{L}$ ) solution of 4 equimolar amount of iodine (purchased from Aldrich  $\geq 99.99\%$ ) was added at –103 to –106 °C under Ar gas flow. The reaction mixture turned from blue to green, then to purple to give the biradical **1cf**. The tube was stored in a liquid nitrogen prior to the ESR measurement. Analogous procedure

was used for preparation of samples for SQUID magnetometry.<sup>13</sup>

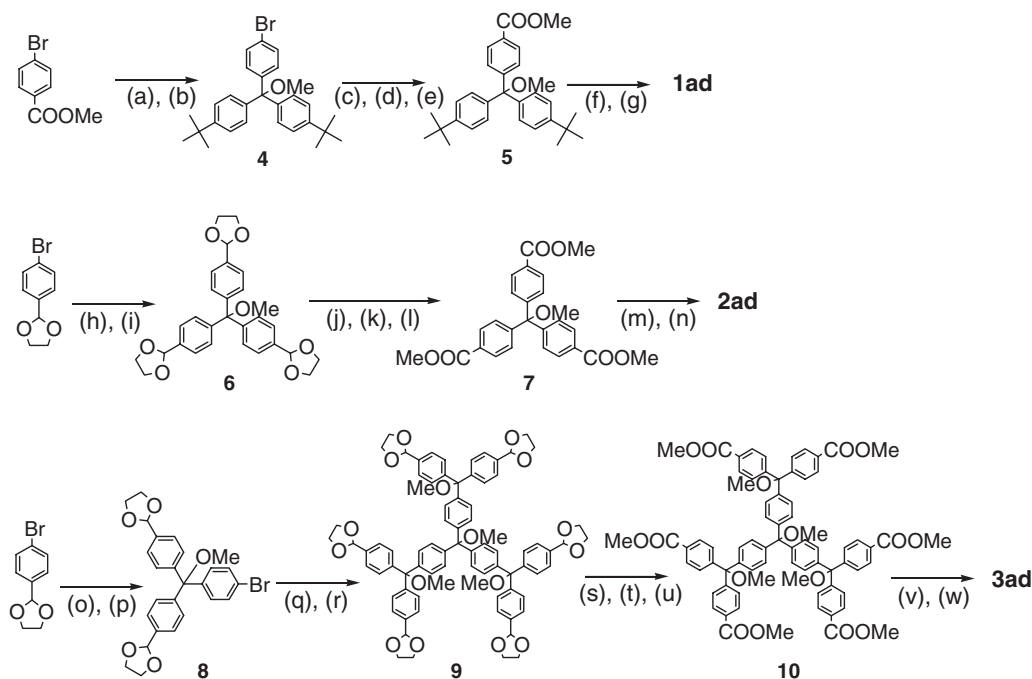
#### Measurements

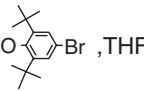
Cyclic and rotating disk voltammetry were carried out with a BAS 100B/W electrochemical analyzer using the dichloromethane solution of 0.1 M tetrabutylammonium tetrafluoroborate and eight equiv of tetrabutylammonium hydroxide (10% methanol solution) under an argon atmosphere. A platinum working electrode and a commercial Ag/AgCl electrode as the reference were used. The formal potential of the ferrocene/ferrocenium couple was 0.43 V vs. this reference electrode. ESR spectra were taken using a JEOL JES-2XG and Bruker EMX ESR spectrometer. IR, NMR, mass, and UV spectra were measured with JASCO FT/IR-410, JEOL NMR 500L or Bruker NMR AVANCE-600, Shimadzu GC-MS 17A, and JASCO V-550 spectrometer, respectively. Magnetic measurements were carried out on MPMS5S (Quantum Design) SQUID magnetometer. All samples for magnetic measurement were handled at low temperature, as described elsewhere.<sup>13</sup>

## RESULTS AND DISCUSSION

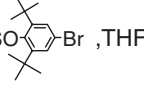
*p*-Bromo-*tert*-butylbenzene was lithiated with *n*-butyllithium, and coupled with methyl *p*-bromobenzoate to yield a triphenylmethane structure.<sup>24,25</sup> The residual bromo group was converted to the ester group by the following formylation, oxidation, and esterification, and the 4-bromo-2,6-di-*tert*-butylphenols were inserted to the ester of **5** to form a galvinoxyl skeleton of **1ad**. **2ad** was similarly prepared by forming a triphenylmethane structure, esterification, and formation of three terminal galvinoxyl groups. The dendritic triphenylmethane structure of **3ad** was formed by the following convergent method. Methyl *p*-bromobenzoate was coupled with the *p*-bromobenzaldehyde protected with cyclic acetal, to yield the bromo triphenylmethane derivative **8**. Three bromo triphenylmethane derivatives **8** were coupled with dimethylcarbonate to give the dendritic triphenylmethane, and its six terminal groups were converted to the hydroxyl groups. The total yield of **3ad** reached 19%.

NMR and other spectroscopies supported the structures of **1ad**, **2ad**, and **3ad**. For example, the coupling between the two protons of the quinone structure was attributed to the hydroxyl group(s) (see Experimental Section). The *tert*-butyl groups of the quinone groups of **2ad** and **3ad** were well resolved into two signals ascribed to the *tert*-butyl group near the hydroxylphenyl group and to the *tert*-butyl group far from the hydroxylphenyl group. The UV/vis spectra of **1ad**, **2ad**, and **3ad** showed a strong absorption

**Reagents**for **1ad**

- (a)  $n$ -BuLi, , THF  
 (b)  $\text{CH}_3\text{I}$ , NaH, THF (c)  $n$ -BuLi, DMF, THF  
 (d)  $\text{NaClO}_2$ ,  $\text{H}_2\text{NSO}_3\text{H}$  (e) MeOH,  $\text{H}_2\text{SO}_4$   
 (f)  $n$ -BuLi, TMSO--Br, THF  
 (g) HCl, THF, MeOH

for **2ad**

- (h)  $n$ -BuLi, MeOCOOME, THF (i)  $\text{CH}_3\text{I}$ , NaH, THF  
 (j)  $\text{H}_2\text{O}$ ,  $p$ -TsOH, acetone (k)  $\text{NaClO}_2$ ,  $\text{H}_2\text{NSO}_3\text{H}$   
 (l) MeOH,  $\text{H}_2\text{SO}_4$   
 (m)  $n$ -BuLi, TMSO--Br, THF  
 (n) HCl, THF, MeOH

for **3ad**

- (o)  $n$ -BuLi, MeOOC-, THF  
 (p)  $\text{CH}_3\text{I}$ , NaH, THF (q)  $n$ -BuLi, MeOCOOME, THF  
 (r)  $\text{CH}_3\text{I}$ , NaH, THF (s)  $\text{H}_2\text{O}$ ,  $p$ -TsOH, acetone  
 (t)  $\text{NaClO}_2$ ,  $\text{H}_2\text{NSO}_3\text{H}$  (u) MeOH,  $\text{H}_2\text{SO}_4$   
 (v)  $n$ -BuLi, TMSO--Br, THF  
 (w) HCl, THF, MeOH

**Scheme 2.**

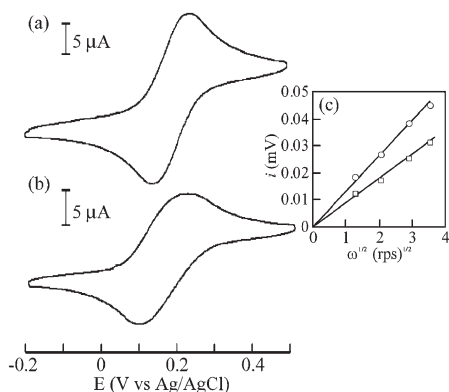
( $\lambda_{\text{max}} = ca. 410 \text{ nm}$ ) ascribed to the quinone structure. The mass spectrum of **3ad** revealed a single peak, which is characteristic of a dendrimer with a regular structure.

The galvinoxyl terminal groups of **1ad**, **2ad**, and **3ad** were electrochemically analyzed. Cyclic voltammetry of **1ae**, **2ad**, and **3ae** in the basic dichloromethane solution showed one reversible redox wave at 0.2 V (Figure 1), indicating the redox reaction between the galvinoxylate anions and the galvinoxyl radicals and the chemical stability of the galvinoxyl

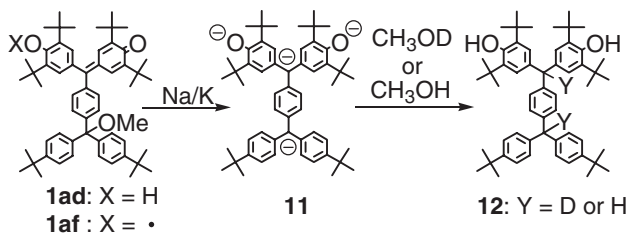
radicals in solution at room temperature. The galvinoxylate anions, **2ae** and **3ae**, were oxidized using rotating disk voltammetry. The electron transfer number per molecule in the oxidation was estimated from the Levich plots:<sup>26</sup> The numbers of 3 and 6, for **2ae** and **3ae**, respectively, clearly indicated the equivalent oxidation of all galvinoxylate anions of **2ae** and **3ae**.

The galvinoxyl radicals, **1af**, **2af**, and **3af**, were prepared by heterogeneously treating the toluene solutions of **1ad**, **2ad**, and **3ad** with an aqueous alkaline ferricyanide solution.<sup>27</sup> The organic layer turned from





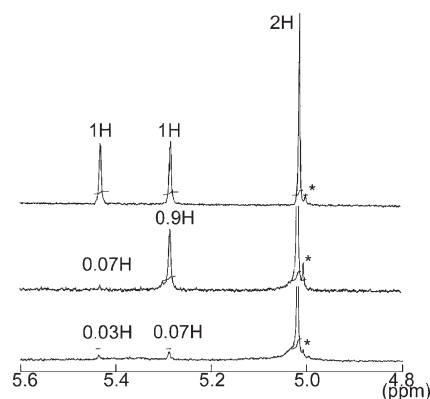
**Figure 1.** Cyclic voltammograms (a) and (b) for **1ae** and **3ae**, respectively, and the Levich plots (c) for **1ae** (○) and **3ae** (□) in  $\text{CH}_2\text{Cl}_2$  with 0.1 M  $(\text{C}_4\text{H}_9)\text{NBF}_4$  and  $(\text{C}_4\text{H}_9)\text{NOH}$  (scanning rate = 50 mV).



**Scheme 3.**

blue to dark brown during the oxidation, and the galvinoxyls were isolated as brownish powders, of which the half-life was estimated by the ESR signal intensity to be longer than 1 month at room temperature in air. The radical content was measured by NMR spectroscopy. The methoxy groups non-conjugated but coupled with the galvinoxyl radicals gave a broad and high-field shifted peak.<sup>18</sup> The radical content based on the integral ratio of the methoxy groups in the hydrogalvinoxyl and in the galvinoxyl radical derivative was almost 100% for **1af**, **2af**, and **3af**. The UV/vis spectra of **1af**, **2af**, and **3af** gave absorption peaks at 477–485 nm ascribed to the galvinoxyl radicals. The ESR spectrum for **1af** showed a 5-line hyperfine structure at  $g = 2.0041$  attributed to the galvinoxyl radical, while it gave a complicated hyperfine structure and a broadened signal due to the intramolecular spin-exchange with the neighboring radicals for **2af** and **3af**, respectively.

**1ad** was reduced with a Na/K alloy to the tetraanion **11** for preparation of the biradical precursor:<sup>28</sup> The hydrogalvinoxyl group was reduced to the galvinoxylate anion, and the galvinoxyl skeleton was converted to a diphenyl carbanion. The methoxy group substituted to the central carbon of triphenylmethane was also eliminated with the Na/K alloy to form a carbanion. During the reduction, the reaction mixture immediately turned from yellow to blue, then to red after 23 h

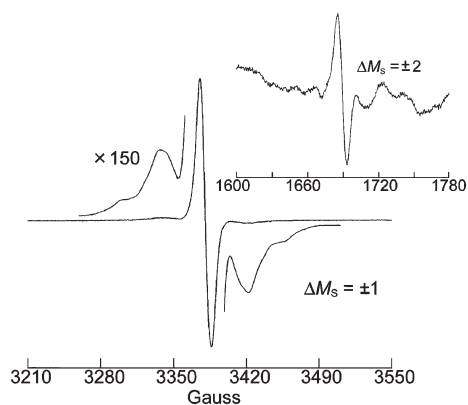


**Figure 2.** NMR spectra (the  $\text{Ph}_3\text{C-Y}$  region) for the quenched compounds **12**. Top: The hydrogalvinoxyl **1ad** was reduced and quenched with  $\text{CH}_3\text{OH}$ . Middle: The hydrogalvinoxyl **1ad** was reduced and quenched with  $\text{CH}_3\text{OD}$ . Below: The galvinoxyl radical **1af** was reduced and quenched with  $\text{CH}_3\text{OD}$ .

at 195 K. The resultant anion was quenched to **12** with  $\text{CH}_3\text{OD}$  to confirm formation of the tetraanion **11**. **11** was also quenched to **12** with  $\text{CH}_3\text{OH}$  as the control sample. The  $\text{Ph}_3\text{C-R}$  region of the quenched sample **12** was studied by NMR spectroscopy. The carbanion on the bis(phenoxyl)phenylmethane moiety was partially hydrated with the phenolic proton (Figure 2, top and middle). On the other hand, the galvinoxyl radical **1af** was similarly reduced using the Na/K alloy in THF to the tetraanion **11** with a color change of the solution from brown to blue, then to deep red after 10 h. This tetraanion **11** was quenched to the totally deuterated triphenylmethane with  $\text{CH}_3\text{OD}$  (Figure 2, bottom). These results indicated that the reduction of the galvinoxyl radical **1af** with the Na/K alloy was desirable for the equivalent tetraanion **11** generation.

The stable decaanion and docosaanion were also prepared from the corresponding galvinoxyl radical **2af** and **3af** with the Na/K alloy in THF, respectively. The decaanion and docosaanion converted from **2af** and **3af** were quenched with  $\text{CH}_3\text{OD}$  to the deuterated triphenylmethane, thus supporting the equivalent anion formation.

The biradical or the galvinoxyl-combined triphenylmethyl radical **1cf** was generated, as described below.<sup>29,30</sup> The galvinoxyl radical **1af** was first generated by oxidation with aqueous ferricyanide, and then reduced to the tetraanion **11** with the Na/K alloy in  $\text{THF-d}_8$  at 283 K for 24 h. The deeply red colored solution of the tetraanion **11** was filtered and transferred to an ESR tube. The addition of the THF solution of 4 equimolar amount of iodine at 170 K yielded **1cf** along with a solution color change from blue to green, then to purple. The ESR spectrum of **1cf** at 140 K showed a structured signal at  $g = 2.0043$  (Figure 3). The zero-field parameters ( $|D/hc| \approx 0.007 \text{ cm}^{-1}$  and



**Figure 3.** ESR spectrum of the biradical **1cf** in THF-*d*<sub>8</sub> at 140 K.

$|E/hc| \approx 0 \text{ cm}^{-1}$ ) are relatively large compared to the values for similar Yang's biradical ( $|D/hc| = 0.0033 \text{ cm}^{-1}$  and  $|E/hc| = 0.00022 \text{ cm}^{-1}$ );<sup>31</sup> this may suggest a spin-delocalization of the galvinoxyl radical into the triphenylmethane moiety.<sup>32</sup> A  $\Delta M_S = \pm 2$  forbidden transition was clearly observed for the biradical **1cf** at the half-field (Inset of Figure 3), which indicated the triplet state for **1cf**.<sup>33</sup>

An attempt was made to generate the tetradical **2cf** and the octaradical **3cf** by similar treatment of **2af** and **3af** with the Na/K alloy and iodine. However, the ESR spectra showed no zero-field splitting and no  $\Delta M_S = \pm 2$  forbidden transition absorption. The fatal spin defect could not be avoided in the tetra- and octaradical formations. For the preparation **2cf** and **3cf**, a new procedure for the radical generation is crucial.

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