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Redox-Based Spin Diversity in a 6-Oxophenalenoxyl System: Generation, ESR/ENDOR/TRIPLE, and Theoretical Studies of 2,5,8-Tri-*tert*-butylphenalenyl-1,6-bis(olate) Salts

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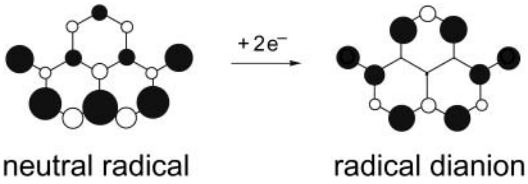
ABSTRACT



Novel open-shell molecular salts, 2,5,8-tri-*tert*-butylphenalenyl-1,6-bis(olate) salts, were designed on the basis of the 6-oxophenalenoxyl system and generated by the chemical reduction of 6-hydroxyphenalenone derivatives. ESR/ENDOR/TRIPLE measurements and DFT calculations provide unequivocal determination of the structure and spin density distribution, which demonstrate redox-based spin diversity of the 6-oxophenalenoxyl system.

Creation of new π-electronic systems with highly delocalized unpaired electrons can afford a fundamental insight into not only the intrinsic nature of the π-spin distribution but also potentials of novel organic functionality. The understanding of the π-spin distribution is the best starting point for the design and preparation of molecule-based magnetic materials.[1] Thus, the 6-oxophenalenoxyl derivatives we recently prepared can be envisioned as materials for a variety of organic spin-bearing sources.[2,3] Interestingly, this neutral radical is unique in exhibiting both an extensively spin-delocalized and highly spin-polarized nature similar to that of the phenalenyl system, while the topology of the spin density distribution sharply contrasts with that of the phenalenyl system.[3a,b] This remarkable difference in topological symmetry of the π-electron network in 6-oxophenalenoxyl derivatives is ascribable to heteroatomic perturbation such

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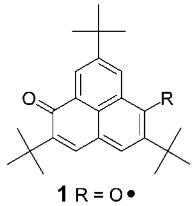
(1) For recent overviews of organic-based magnetic materials, see, e.g.: (a) *Molecular Magnetism*; Itoh, K., Kinoshita, M., Eds.; Kodansha, and Gordon and Breach Science Publishers: Tokyo, 2000; pp 1−347. (b) *Magnetic Properties of Organic Materials*; Lahti, P. M., Ed.; Marcel Dekker: New York, 1999; pp 1−728. (c) Kahn, O., Ed.; *Mol. Cryst. Liq. Cryst.* **1999**, *334/335*, 1−712/1−706. (d) Itoh, K., Miller, J. S., Takui, T., Eds.; *Mol. Cryst. Liq. Cryst.* **1997**, *305/306*, 1−586/1−520.

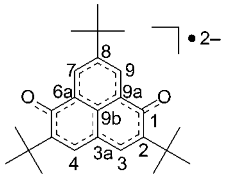
(2) For overviews of the stable neutral radicals, see, e.g.: (a) Forrester, A. R.; Hay, J. M.; Thomson, R. H. *Organic Chemistry of Stable Free Radicals*; Academic Press: London and New York, 1968. (b) Rozantsev, E. G. *Free Nitroxyl Radicals*; Plenum Press: New York and London, 1970. (c) Aurich, H. G. In *Nitrones, Nitronates and Nitroxides*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1989; Chapter 4. (d) Volodarsky, L. B.; Reznikov, V. A.; Ovcharenko, V. I. *Synthetic Chemistry of Stable Nitroxides*; CRC Press: Boca Raton, FL, 1994. (e) Iwamura, H.; Koga, N. *Acc. Chem. Res.* **1993**, *26*, 346−351.

10.1021/ol020041v CCC: $22.00

as the delocalization nature due to the two oxygen atoms introduced into the *neutral* phenalenyl skeleton. Thus, an interesting query has arisen as to the electronic spin structure of the redox state of this system. In this paper, we focus on the generation and ESR detection of the radical dianion **4**$^{\bullet 2-}$, as the first example of the open-shell molecule showing the reversible topological switching of the spin density distribution in the spin-delocalized molecular system by controlling redox processes. This spin switching characteristic is termed redox-based spin diversity.[4,5]



1 R = O•
2 R = OH
3 R = O$^-$



4$^{\bullet 2-}$

To investigate the redox chemistry of the 6-oxophenalenoxyl system, we carried out the cyclic voltammetry (CV) of the tetraethylammonium salt of the 6-hydroxyphenalenone, (Et$_4$N$^+$)·**3**, which was prepared as a stable solid from **2**[3b] by the treatment of 1 equiv of NaOMe followed by Et$_4$NCl in THF−MeOH.[6] CV measurements in CH$_3$CN at room temperature have given a single reversible oxidation wave (−0.30 V) and a single reversible reduction wave (−2.39 V), indicating the high stability of the neutral radical **1** and radical dianion species **4**$^{\bullet 2-}$ (Figure 1). These results have encouraged us to generate **4**$^{\bullet 2-}$ by chemical reduction and to characterize its stability and electronic structure.

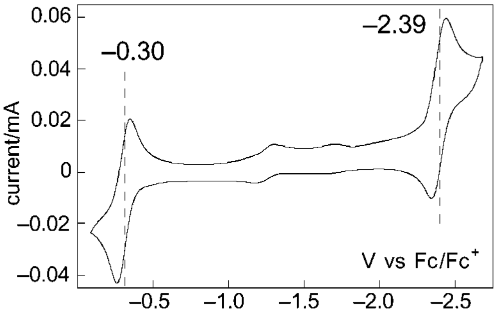


Figure 1. Cyclic voltammogram for (Et$_4$N$^+$)·**3** in a CH$_3$CN solution (10 mM) containing Bu$_4$NClO$_4$ (0.1 M) at room temperature versus a Ag/10 mM AgNO$_3$ in CH$_3$CN reference electrode. A 1.6 mm diameter gold electrode was used as the working electrode, and platinum wire was used as the counter electrode. The sweep rate was 0.2 V/s. Final results were calibrated with the ferrocene/ferrocenium couple.

The dipotassium salt of the radical dianion (2K$^+$)·**4**$^{\bullet 2-}$ was generated as a deep green solution by the treatment of the 6-hydroxyphenalenone derivative **2**[3b] with potassium mirror (**Caution !**) in a degassed diglyme solution (1.0 × 10^{-3} M) in a sealed tube, which showed well-resolved hyperfine ESR signals (Figure 2A).[7] The decrease in these signal intensities was not observed for a year at room temperature in a sealed tube, indicative of the high stability in the degassed solution. The spectral simulations were satisfactorily made on the basis of the two sets of isotropic hyperfine coupling constants (hfccs) of the four protons on the phenalenyl skeleton obtained by ^{1}H-ENDOR spectroscopy (Figure 2B)[8] with the additional two equivalent hfccs (±0.025 mT) that are attributed to the coupling with ^{39}K nuclear spins (Figure 2D).[9] The relative signs of the hfccs due to two kinds of protons were unequivocally found to be equal by invoking ^{1}H-TRIPLE resonance measurements (Figure 2C). For the confirmation of the spin coupling with the two counter-

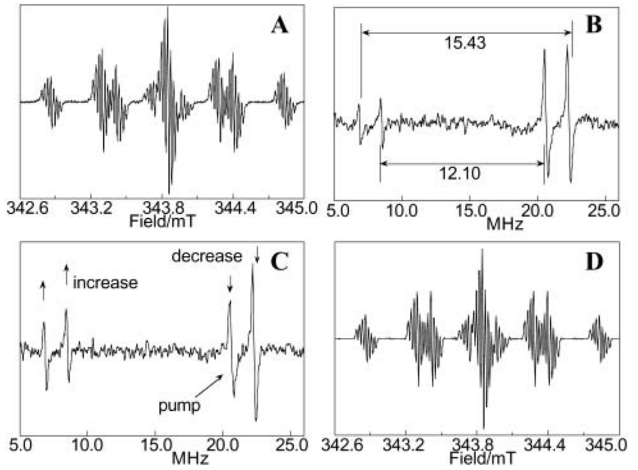


Figure 2. Observed hyperfine ESR spectrum (A), ^{1}H-ENDOR spectra (B), and ^{1}H-TRIPLE (C; pump frequency, 20.65 MHz) spectra for (2K$^+$)·**4**$^{\bullet 2-}$ generated from **2** with K mirror in a diglyme solution (1 × 10^{-3} M) at 290 K and a simulated spectrum (**D**). Microwave frequency used for ESR measurement was 9.6455240 GHz. Observed *g*-value is 2.0037.

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(3) (a) Hatanaka, K.; Morita, Y.; Ohba, T.; Yamaguchi, K.; Takui, T.; Kinoshita, M.; Nakasuji, K. *Tetrahedron Lett.* **1996**, *37*, 877−880. (b) Morita, Y.; Ohba, T.; Haneda, N.; Maki, S.; Kawai, J.; Hatanaka, K.; Sato, K.; Shiomi, D.; Takui, T.; Nakasuji, K. *J. Am. Chem. Soc.* **2000**, *122*, 4825−4826. (c) Morita, Y.; Maki, S.; Fukui, K.; Ohba, T.; Kawai, J.; Sato, K.; Shiomi, D.; Takui, T.; Nakasuji, K. *Org. Lett.* **2001**, *3*, 3099−3102. (d) Morita, Y.; Kawai, J.; Haneda, N.; Nishida, S.; Fukui, K.; Nakazawa, S.; Shiomi, D.; Sato, K.; Takui, T.; Kawakami, T.; Yamaguchi, K.; Nakasuji, K. *Tetrahedron Lett.* **2001**, *42*, 7991−7995.

(4) Redox-based spin conversions controlled by the π-topological symmetry of nonbonding MOs have been studied in high-spin carbenes chemistry; see: (a) Matsushita, M.; Nakamura, T.; Momose, T.; Shida, T.; Teki, Y.; Takui, T.; Kinoshita, T.; Itoh, K. *J. Am. Chem. Soc.* **1992**, *114*, 7470−7475. (b) Nakamura, T.; Momose, T.; Shida, T.; Sato, K.; Nakazawa, S.; Kinoshita, T.; Takui, T.; Itoh, K.; Okuno, T.; Izuoka, A.; Sugawara, T. *J. Am. Chem. Soc.* **1996**, *118*, 8684−8687 and references therein.

(5) “Spin diversity” has been used in different terms; see: (a) Shultz, D. A.; Bodnar, S. H.; Vostrikova, K. E.; Kampf, J. W. *Inorg. Chem.* **2000**, *39*, 6091−6093. (b) Depperman, E. C.; Bodnar, S. H.; Vostrikova, K. E.; Shultz, D. A.; Kirk, M. L. *J. Am. Chem. Soc.* **2001**, *123*, 3133−3134.

(6) Selected physical data: (Et$_4$N$^+$)·**3**, mp 253−255 °C dec; ^{1}H NMR (270 MHz, DMSO-d_6) δ 1.12−1.41 (m, 12), 1.37 (s, 18), 1.41 (s, 9), 3.19 (q, 8, J = 7.3 Hz), 7.34 (s, 2), 7.46 (s, 2); IR (KBr) 2947, 1508, 1498 cm^{-1}; Anal. Calcd for (C$_{33}$H$_{51}$NO$_2$)(H$_2$O)$_{1.1}$: C, 77.17; H, 10.44; N, 2.73. Found: C, 77.08; H, 10.24; N, 2.91.

cations, we have generated the disodium salt of the radical dianion, (2Na^{+})·**4**$^{\bullet 2-}$, by the reduction of **2**[3b] with sodium mirror (**Caution !**). Figure 3 shows a resolved hyperfine ESR spectrum (A) observed in a degassed diglyme solution (1.0 × 10^{-3} M) and the simulated one (B) based on the consideration of the effect of the two counter sodium cations.[10] These results clearly demonstrate that the potassium or sodium mirror based reduction of **6** gives the 2,5,8-tri-*tert*-butylphenalenyl-1,6-bis(olate) salt as single paramagnetic species in which an unpaired electron on the phenalenyl-bis(olate) skeleton couples with the nuclear spin of the two potassium or sodium cations, although the structure and equilibration nature of the ion pair(s) are uncertain.

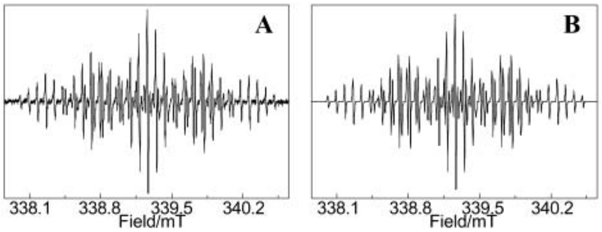


Figure 3. Observed hyperfine ESR spectrum (A, 290 K) for (2Na^{+})·**4**$^{\bullet 2-}$ generated from **2** with Na mirror in a diglyme solution (1 × 10^{-3} M) at 253 K and a simulated spectrum (B). Microwave frequency used for ESR measurement was 9.5178404 GHz. Observed *g*-value is 2.0037.

Calculations of the results of the π-spin densities in terms of a local spin density functional theory were made using Gaussian 94 with the UBLYP/6-31G*//UBLYP/6-31G* method and indicated that the π-spin densities on C3,C4 and C7,C9 in **4**$^{\bullet 2-}$ were almost the same values, which led to an ambiguity of proton assignments (Figure 4, contrasting with the neutral radical **1**).[11] Thus, to fully assign the four protons on the phenalenyl skeleton, we carried out the incorporation of a deuterium atom into the phenalenyl skeleton, and designed **7**$^{\bullet 2-}$. The regiospecific deuteration was achieved by the reduction of the phenalanone **5**[3b] with LiAlD$_4$ (>98 atom % D), followed by the demethylation by an excess amount of LiI in *N*,*N*-dimethylacetamide, dehydration, and aerobic oxidation, to afford the regiospecifically deuterated 6-hydroxyphenalenone **6**.[12] This radical dianion precursor was first converted into the potassium salt by *tert*-BuOK in THF, and then this salt was treated with potassium mirror in a degassed diglyme solution (1.0 × 10^{-3} M) in a sealed tube to yield the radical dianion (2K^{+})·**7**$^{\bullet 2-}$.[13]

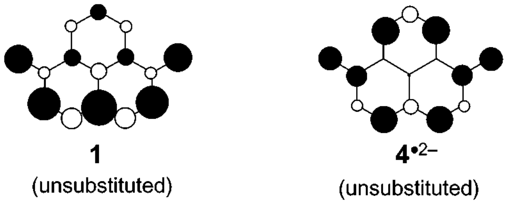
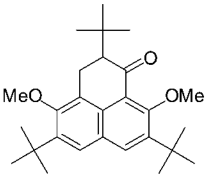


Figure 4. π-Spin density distribution of **1** and **4**$^{\bullet 2-}$ calculated by a local spin density functional theory using Gaussian 94 with the UBLYP/6-31G*//UBLYP/6-31G* method. Vacant and filled circles denote negative and positive π-spin densities, respectively.[11]



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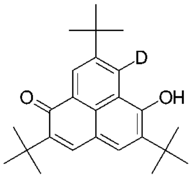

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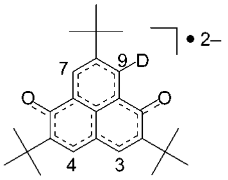

7$^{\bullet\, 2-}$

Figure 5 shows a well-resolved hyperfine ESR spectrum (A) and a simulated one (B) based on the calculated π-spin densities on C3,C4 and C7,C9 with a reasonable gyromagnetic ratio (γ_D/γ_H = 4.107/26.75) for the mixture of (2K^{+})·**7**$^{\bullet 2-}$ (98%) and (2K^{+})·**4**$^{\bullet 2-}$ (2%).[14] These observed and

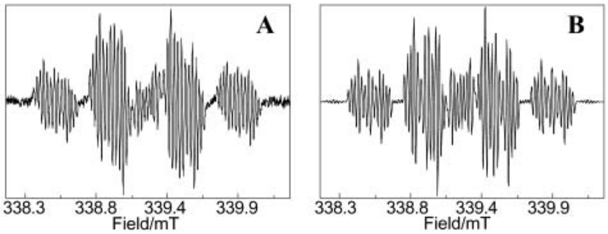

Figure 5. Observed hyperfine ESR spectrum (A) for (2K^{+})·**7**$^{\bullet 2-}$ generated from the potassium salt of **6** with K mirror in a diglyme solution (1 × 10^{-3} M) at 290 K and a simulated spectrum (B). Microwave frequency used for ESR measurement was 9.5160733 GHz. Observed *g*-value is 2.0037.

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(7) Potassium mirror based reduction of **2** was also conducted in a THF or DME solution, but the resulting products were solidified in the ESR-tubes. Interestingly, in the presence of dicyclohexano-18-crown-6 in a DME solution, the potassium mirror based reduction of **2** yielded a deep green solution, which showed hyperfine ESR signals reasonably assignable to **4**$^{\bullet 2-}$ with the very small hfcc arising from interaction with the counterion K^{+}; see Supporting Information.

(8) ENDOR resonance signals of the ^{39}K nuclear spin could not be observed, since they are expected to appear outside the spectrometer frequency range (ν_{39K} = 0.680 MHz). The intensity of the ENDOR resonance signals of the protons on the three *tert*-butyl groups was very weak, although the reason remains obscure.

(9) This spectral simulation was conducted with taking account of ^{13}C-hyperfine couplings. The detailed calculation and assignments are underway.

(10) This result is also supported by the ^{1}H-ENDOR and ^{1}H-TRIPLE spectra for (2Na^{+})·**4**$^{\bullet 2-}$, generated from (Na^{+})·**3** with Na mirror in a diglyme solution (1.0 × 10^{-3} M) at 290 K.; see Supporting Information.

(11) Detailed calculated results of the π-spin density distributions for **1** and **4**$^{\bullet 2-}$ by the UBLYP/6-31G*//UBLYP/6-31G* and SVWN/6-31G**//SVWN/6-31G** methods are given in Supporting Information.

(12) Mp 235−236 °C (sublimation); TLC R_f = 0.61 (2:1 hexane/ethyl acetate); ^{1}H NMR (270 MHz, CDCl$_3$) δ 1.44 (s, 9), 1.48 (s, 9), 1.57 (s, 9), 6.05 (s, 1), 7.57 (s, 1), 7.66 (s, 1), 8.31 (s, 0.5), 8.75 (s, 0.5); ^{1}H NMR (270 MHz, CDCl$_3$ with a catalytic amount of CF$_3$COOH) δ 1.49 (s, 9), 1.52 (s, 18), 7.75 (brs, 2), 8.68 (brs, 1); IR (KBr) 3500−3000, 2958, 1560 cm^{-1}; EI-MS, *m/z* 365 (M^{+}, 25%), 308 (M^{+} − C$_4$H$_9$, 100%). Anal. Calcd for C$_{25}$H$_{31}$DO$_2$: C, 82.15; H, 8.55; D, 0.55; N, 0.00. Found: C, 81.82; H, 8.54; D, 0.55; N, 0.00. The deuteration ratio was estimated to be very high by the result of the EI-MS measurement.

simulated ESR spectra clearly elucidate the structure of the radical dianion $\mathbf{7}^{\bullet 2-}$ and full assignment of the four protons on the phenalenyl skeleton. The observed and theoretically calculated values of the hfccs for the $(2K^+)\cdot\mathbf{4}^{\bullet 2-}$, $(2Na^+)\cdot\mathbf{4}^{\bullet 2-}$, and $(2K^+)\cdot\mathbf{7}^{\bullet 2-}$ were summarized in Table 1. Agreements between the experimental and theoretical values are satisfactory. Furthermore, a small but significant difference of the hfccs on C3−H and C4−H between $(2K^+)\cdot\mathbf{4}^{\bullet 2-}$ and $(2Na^+)\cdot\mathbf{4}^{\bullet 2-}$ reflects the electronic structure and/or equilibration nature of the corresponding ion pairs.[15]

Table 1. Observed and Calculated Proton and Counter-Cation Hfccs for $(2K^+)\cdot\mathbf{4}^{\bullet 2-}$, $(2Na^+)\cdot\mathbf{4}^{\bullet 2-}$, and $(2K^+)\cdot\mathbf{7}^{\bullet 2-}$ [a]

	A_H/mT			
	H(3, 4)	H(7 and/or 9)	D(9)	^{39}K or ^{23}Na
$(2K^+)\cdot\mathbf{4}^{\bullet 2-}$	−0.434[b]	−0.551[b]		±0.025[b]
	−0.432[c]	−0.550[c]		
$(2Na^+)\cdot\mathbf{4}^{\bullet 2-}$	−0.447[b]	−0.554[b]		±0.083[b]
	−0.444[c]	−0.551[c]		+0.081[c]
$(2K^+)\cdot\mathbf{7}^{\bullet 2-}$	−0.434[b]	−0.551[b]	−0.085[b]	±0.025[b]
	(−0.478)[d]	(−0.508)[d]	(−0.084)[d]	

[a] The relative signs of the hfccs were determined in terms of ^{1}H-TRIPLE spectroscopy. [b] The hfccs were determined by ESR spectra in a diglyme solution at 290 K and spectral simulation. [c] The hfccs were determined by ^{1}H-ENDOR spectra in a diglyme solution at 290 K. [d] These hfccs were calculated for $\mathbf{4}^{\bullet 2-}$ by using Guassian 94 with UBLYP/6-31G*//UBLYP/6-31G* method with the help of McConnell's equation ($Q = -2.70$ mT) and gyromagnetic ratio ($\gamma_D/\gamma_H = 4.107/26.75$).

A novel radical dianion $(2K^+ \text{ or } 2Na^+)\cdot\mathbf{4}^{\bullet 2-}$ was designed and successfully generated by the reduction of **2** with potassium or sodium mirror, respectively. Our elaborate ESR/ENDOR/TRIPLE measurements and calculations confirmed that the topological symmetry of the π-electron network in the radical dianion system is in great contrast with that of the neutral radical system **1**, demonstrating the redox-based spin diversity nature of the 6-oxophenalenoxyl system (Figure 4).[16]

This study contributes to the new molecular design for novel organic open-shell systems exhibiting controllable magnetic properties such as organic molecular battery by excess electrons. Moreover, the unique property of the 6-oxophenalenoxyl system continues to challenge our understanding of novel π-electronic systems through which we hope to gain further insight into the interplay between the highly delocalized nature of the unpaired electron and charge fluctuation.[17,18]

Acknowledgment. This work was supported by Grant-in-Aid for Scientific Research on Priority Area "Delocalized π-Electronic Systems" (No. 297) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Supporting Information Available: Experimental procedures and full characterizations of new compounds, **3**, $\mathbf{4}^{\bullet 2-}$, **6** and $\mathbf{7}^{\bullet 2-}$, hyperfine ESR spectrum of $(2K^+)\cdot\mathbf{4}^{\bullet 2-}$ in DME in the presence of dicyclohexano-18-crown-6, ^{1}H-ENDOR and ^{1}H-TRIPLE spectra of $(2Na^+)\cdot\mathbf{4}^{\bullet 2-}$ in diglyme, and the calculated results of the spin density distributions and charge fluctuation of the radical dianion $\mathbf{4}^{\bullet 2-}$ calculated by the DFT methods by using Gaussian 94 with the UBLYP/6-31G*//UBLYP/6-31G* and SVWN/6-31G**//SVWN/6-31G** methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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[13] D−H exchange reaction was greatly suppressed by the derivatization of phenolic proton into potassium salt before reduction with potassium mirror. Potassium mirror based reduction of **6** gave an about 9:1 mixture of $\mathbf{7}^{\bullet 2-}$ and $\mathbf{4}^{\bullet 2-}$ within 24 h.

[14] ESR simulation based on this isomeric ratio showed the best agreement with the observed ESR spectrum, which shows no contradiction to the high deuteration ratio of **6**.

[15] Electronic structures of radical anions are correlated with some intrinsic properties of the respective counterions; see: Lubitz, W.; Plato, M.; Möbius, K.; Biehl, R. *J. Phys. Chem.* **1979**, *83*, 3402−3413.

[16] Spin density distributions of the hexa-*tert*-butyl substituted tribenzodecacyclenyl radical and its redox states exhibit a topology similar to that of the phenalenyl radical system; see: Kubo, T.; Yamamoto, K.; Nakasuji, K.; Takui, T.; Murata, I. *Bull Chem. Soc. Jpn.* **2001**, *74*, 1999−2009.

[17] The following results of the two calculation methods indicate that the two anion charges of the radical dianion $\mathbf{4}^{\bullet 2-}$ are also delocalized over the phenalenyl skeleton as well as on the two oxygen atoms, which is likely to produce its high stability. UBLYP/6-31G*//UBLYP/6-31G* method: C1, C6, +0.2930; C2, C5, −0.2212; C3, C4, −0.2528; C7, C9, −0.1895; C8, −0.1285; C3a, +0.1765; C6a, C9a, +0.0481; C9b, −0.0221; O1, O6, −0.6905. SVWN/6-31G**//SVWN/6-31G** method: C1, C6, +0.2335; C2, C5, −0.2065; C3, C4, −0.2284; C7, C9, −0.1618; C8, −0.1451; C3a, +0.1366; C6a, C9a, +0.0141; C9b, −0.0108; O1, O6, −0.6413; see Supporting Information.

[18] Interplay between the unpaired electron and the electrical charge plays a key role in properties of electronic structures of radical ions; see refs 4, 15, and the following recent reference: Exner, K.; Cullmann, O.; Vögtle, M.; Prinzbach, H.; Grossmann, B.; Heinze, J.; Liesum, L.; Bachmann, R.; Schweiger, A.; Gescheidt, G. *J. Am. Chem. Soc.* **2000**, *122*, 10650−10660.