

Oxophenalenoxyl: Novel stable neutral radicals with a unique spin-delocalized nature depending on topological symmetries and redox states*

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Abstract: Stable organic open-shell systems have attracted much attention in the field of molecule-based magnetism. We have been exploring novel stable neutral radicals based on a phenalenyl system known as an odd-alternant hydrocarbon π -radical with a highly spin-delocalized nature. Recently, we have designed and synthesized novel oxophenalenoxyl neutral radical systems possessing two oxygen atoms on the phenalenyl skeleton. These systems are unique in comprising some topological isomers depending on the positions of oxygen substituents on the phenalenyl skeleton. The isomers exhibit different topological symmetries of spin density distributions (*spin topological symmetry control*). In addition, two-stage one-electron reductions of these systems give the corresponding radical dianions, which show remarkably different topological symmetries of a spin-delocalized nature from those of the neutral radical systems (*redox-based spin diversity*). In this paper, we discuss the unique spin-delocalized nature of 3-, 4-, and 6-oxophenalenoxyl systems in view of the topological symmetry and redox ability, emphasizing the results from the radical dianion of 4-oxophenalenoxyl system from both experimental and theoretical sides.

Keywords: neutral radicals; spin delocalization; topological symmetry; resonance structure; phenalenyl.

INTRODUCTION

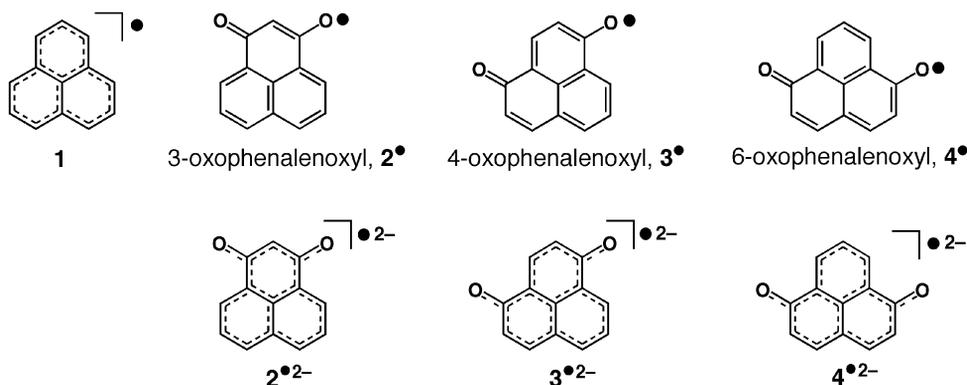
Organic open-shell molecules are known as reaction intermediates in organic synthetic reaction and generally recognized as unstable chemical species [1]. Stabilization and isolation of organic open-shell molecules, however, provided the significant potential as spin sources for molecule-based magnetic materials or prototypes for molecular-spin quantum computers. Actually, some stable organic neutral radicals such as 2,2,5,5-tetramethylpiperidin-1-oxyl (TEMPO) and α -nitronyl nitroxide derivatives gave molecular ferromagnetic materials in the crystalline states [2]. For the progress of molecule-based magnetism and related fields, it is a crucial issue to design and synthesize stable neutral radicals possessing

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novel molecular and electronic structures. In order to synthesize such stable neutral radicals as *material challenges*, we focused on a phenalenyl system **1** known as an odd-alternant hydrocarbon π -radical with a highly spin-delocalized nature. Our chemical modifications of **1** by a steric protection of the reactive sites [3] and by an introduction of nitrogen atoms in the phenalenyl skeleton [4] successfully stabilized phenalenyl-based neutral radicals enough to be isolated. These studies encouraged us to design oxophenalenoxyl systems by an introduction of two oxygen atoms into the phenalenyl skeleton. These systems have spin-delocalized natures depending on topological symmetries of the positions of oxygen substituents (*spin topological symmetry control*) and redox states (*redox-based spin diversity*) (vide infra). In this paper, we discuss the unique spin-delocalized nature of neutral radical and radical dianion derivatives in 3-, 4-, and 6-oxophenalenoxyl systems, 2^{\bullet} – 4^{\bullet} and $2^{\bullet 2-}$ – $4^{\bullet 2-}$, respectively, as a new class of organic neutral radical systems.



RESULTS AND DISCUSSION

Phenalenyl systems

Figure 1 shows the spin density distributions of the phenalenyl **1**, TEMPO, α -nitronylnitroxide derivative, and 1,3-diazaphenalenyl **5** calculated by density functional theory (DFT) calculations [5]. The nitroxide radicals have most of their spin densities on their oxygen and nitrogen atoms, indicating a spin-localized nature (Figs. 1b and 1c). In sharp contrast, **1** has spin densities delocalized on the six α -carbons where the large coefficients of a non-bonding molecular orbital (NBMO) appear (Fig. 1a) [6]. While the highly spin-delocalized nature of **1** causes thermodynamic stability, it is impossible to isolate **1** in the solid state because of low kinetic stability. For stabilizing **1** as an organic spin source, Haddon and coworkers reported the synthesis and isolation of a perchloro-substituted derivative in the crystalline state [7]. Recently, we have successfully isolated the phenalenyl radical in the crystalline state by introduction of *tert*-butyl groups into the β -positions of **1** for steric protection [3]. These modified phenalenyl derivatives also have large spin densities at the α -carbons similar to **1**, undergoing substantially no electronic disturbance by the modification.

We designed novel stable neutral radicals by introduction of nitrogen atoms into the phenalenyl skeleton. A tri-*tert*-butylated derivative of 1,3-diazaphenalenyl **5** was synthesized and isolated as a higher air-stable neutral radical than that of the tri-*tert*-butylated derivative of **1** in the solid state [4]. The electron spin delocalizes at the α -positions with a slight decrease of the spin densities on the nitrogen atoms, indicating a phenalenyl-type spin-delocalized nature (Fig. 1d).

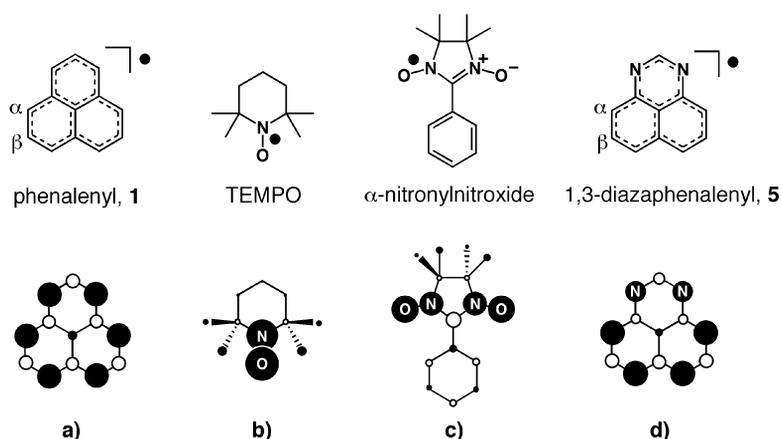


Fig. 1 Chemical structures and spin density distributions calculated at the UBLYP/6-31G(d, p)// UBLYP/6-31G(d, p) level of theory by *Gaussian 03* [5]. (a) Phenalenyl **1**, (b) TEMPO, (c) α -nitronylnitroxide derivative, and (d) 1,3-diazaphenalenyl **5**. Filled and vacant circles denote positive and negative spin densities, respectively.

Oxophenalenoxyl systems

Design and spin topological symmetry control of oxophenalenoxyl neutral radicals

The introduction of two oxygen atoms as oxo and oxyl functional groups into the phenalenyl system provides a unique opportunity for designing novel neutral radicals. Some topological isomers can be designed depending on the positions of oxygen substituents on the phenalenyl skeleton (Fig. 2) [8]. A β,β -substituted isomer possesses a naphthoxyl structure with two extra unpaired electrons, implying a low stability of this system. On the other hand, α,β - and α,α -substituted isomers were designed as monoradical systems. Especially, each of the α,α -isomers is unique in having two tautomeric isomers by an extensive delocalization of an unpaired electron between the two oxygen atoms. Thus, for designing stable neutral radicals, we focused on 1,3-, 1,4-, and 1,6-isomers, which were named as 3-, 4-, and 6-oxophenalenoxyls **2[•]**, **3[•]**, and **4[•]**, respectively.

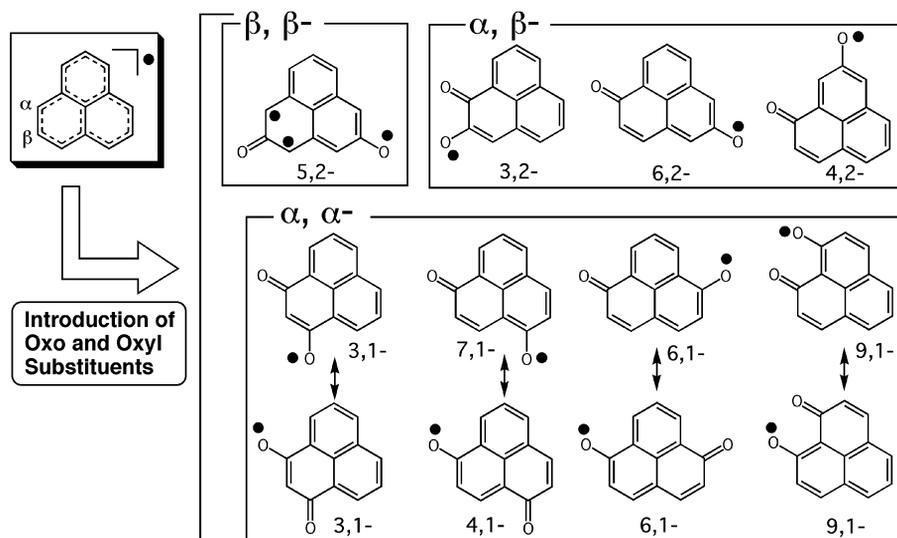


Fig. 2 Molecular design and topological isomers of the oxophenalenoxyl systems.

With these considerations in mind, we designed 3-, 4-, and 6-oxophenalenoxyl derivatives **6a**[•] [9], **7**[•] [8], and **8**[•] [10], respectively. Our ESR/¹H-ENDOR/TRIPLE measurements of these neutral radicals with the help of DFT calculations show that these radicals have most of spin densities at the β-carbons and two oxygen atoms, revealing a remarkable difference between those of **1** and **5** (Fig. 3). Furthermore, each topological isomer shows the different topological symmetries of spin density distributions, which demonstrates *spin topological symmetry control* in monoradical systems for the first time [8].

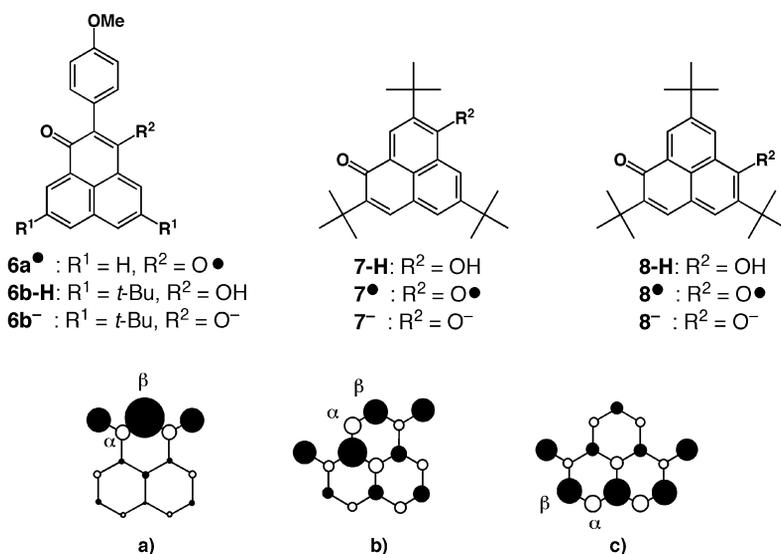


Fig. 3 Spin density distributions of (a) **2**[•], (b) **3**[•], and (c) **4**[•] calculated at the UBLYP/6-31G(d, p)// UBLYP/6-31G(d, p) level of theory by *Gaussian 03* [5]. Filled and vacant circles denote positive and negative spin densities, respectively.

Multi-step redox abilities of 3-, 4-, and 6-oxophenalenoxyl systems

In order to investigate redox abilities of **2**[•], **3**[•], and **4**[•], we carried out the cyclic voltammetry (CV) of the corresponding tetraethylammonium salts of anions in 3-, 4-, and 6-oxophenalenoxyl derivatives (Et₄N⁺)•**6b**⁻, (Et₄N⁺)•**7**⁻, and (Et₄N⁺)•**8**⁻ [11] (Fig. 4). These anions were prepared as stable solids from **6b-H** [12], **7-H** [8], and **8-H** [10a] by a treatment with NaOMe and Et₄NCl in THF–MeOH. CV measurements of (Et₄N⁺)•**7**⁻ and (Et₄N⁺)•**8**⁻ in CH₃CN at 300 K have given single reversible oxidation waves ($E_{1/2}^{\text{ox}} = -0.08$ and -0.30 V) and single reversible reduction waves ($E_{1/2}^{\text{red}} = -2.43$ and -2.39 V), respectively, indicating a high stability of the neutral radicals and radical dianion species (Figs. 4b and 4c). The oxidation potential of (Et₄N⁺)•**8**⁻ are similar to the first reduction potential of chloranil known as a typical organic electron-acceptor, indicating a high electron-accepting ability of the 6-oxophenalenoxyl system **4**[•] [13]. On the other hand, CV measurement of (Et₄N⁺)•**6b**⁻ has given a single reversible reduction wave ($E_{1/2}^{\text{red}} = -2.35$ V) and a single irreversible oxidation wave ($E_{\text{p}}^{\text{ox}} = -0.11$ V), indicating a high stability of radical dianion species and a low stability of the neutral radical (Fig. 4a) [14]. The differences between $E_{1/2}^{\text{red}}$ and $E_{1/2}^{\text{ox}}$ (or E_{p}^{ox}) correspond to the energy gaps between singly occupied molecular orbitals (SOMOs) and the lowest unoccupied molecular orbitals (LUMOs) of the neutral radicals, indicating that the two MOs plays a key role in the redox ability of the oxophenalenoxyl systems. These results demonstrate that the 3-, 4-, and 6-oxophenalenoxyl systems possess two-stage, one-electron redox abilities and high stabilities of their neutral radicals and radical dianions in the solution states except for the neutral radical of the 3-oxophenalenoxyl system.

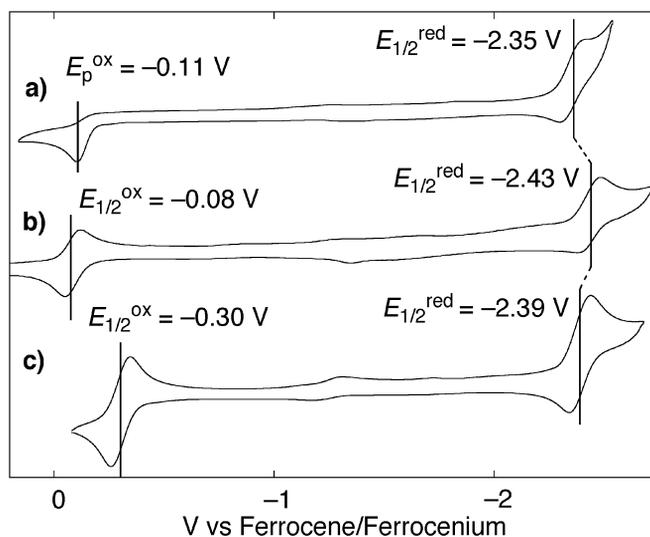
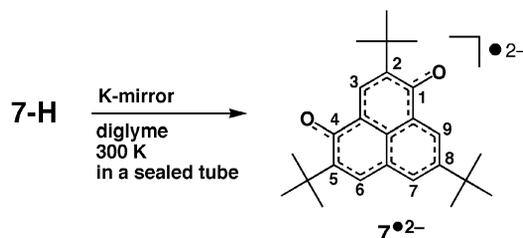


Fig. 4 Cyclic voltammograms for (a) $(\text{Et}_4\text{N}^+) \cdot 6\text{b}^{2-}$ (5 mM; sweep rate, 0.1 V/s), (b) $(\text{Et}_4\text{N}^+) \cdot 7^{2-}$ (3 mM; sweep rate, 0.05 V/s), and (c) $(\text{Et}_4\text{N}^+) \cdot 8^{2-}$ (10 mM; sweep rate, 0.2 V/s) in CH_3CN solution containing Bu_4NClO_4 (0.1 M) at 300 K vs. $\text{Ag}/10 \text{ mM AgNO}_3$ in CH_3CN reference electrode. Final results were calibrated with the ferrocene/ferrocenium coupling.

Redox-based spin diversity of 3-, 4-, and 6-oxophenalenoxyl systems

The result of CV measurements encouraged us to investigate spin structures of the radical dianions 2^{2-} , 3^{2-} , and 4^{2-} . The spin structures of 2^{2-} and 4^{2-} were revealed by the generation and ESR/ ^1H -ENDOR/TRIPLE studies of sterically protected derivatives 6b^{2-} [12] and 8^{2-} [11], respectively. In the present study, we have elucidated spin density distribution of the radical dianion of the 4-oxophenalenoxyl system 3^{2-} by using tri-*tert*-butylated derivative 7^{2-} . The potassium salt $(2 \text{ K}^+) \cdot 7^{2-}$ was generated by a treatment of 4-hydroxyphenalenone **7-H** with potassium mirror in a degassed diglyme solution ($1 \times 10^{-3} \text{ M}$) in a sealed ESR tube at 300 K (Scheme 1). Figure 5 shows (a) an ESR spectrum observed for $(2 \text{ K}^+) \cdot 7^{2-}$ and (b) a simulated one based on five sets of hyperfine coupling constants (hfccs) due to the four protons on the oxophenalenoxyl skeleton obtained by ^1H -ENDOR spectroscopy (Fig. 5c) with the additional two equivalent hfccs ($\pm 0.025 \text{ mT}$) attributed to the ^{39}K nuclear spins. The relative signs of the hfccs were determined by invoking ^1H -TRIPLE measurements (Figs. 5d and 5e). The decrease in the signal intensities was not observed for five years at room temperature in the sealed ESR tube, being indicative of a high stability of $(2 \text{ K}^+) \cdot 7^{2-}$ in the degassed solution. The observed and theoretically calculated values of the hfccs for the $(2 \text{ K}^+) \cdot 7^{2-}$ were summarized in Table 1. Agreement between the experimental and theoretical values is satisfactory. These results have provided an evidence for the generation of $(2 \text{ K}^+) \cdot 7^{2-}$ as a single paramagnetic species, while the structure and equilibration nature of the ion pair(s) are uncertain.



Scheme 1

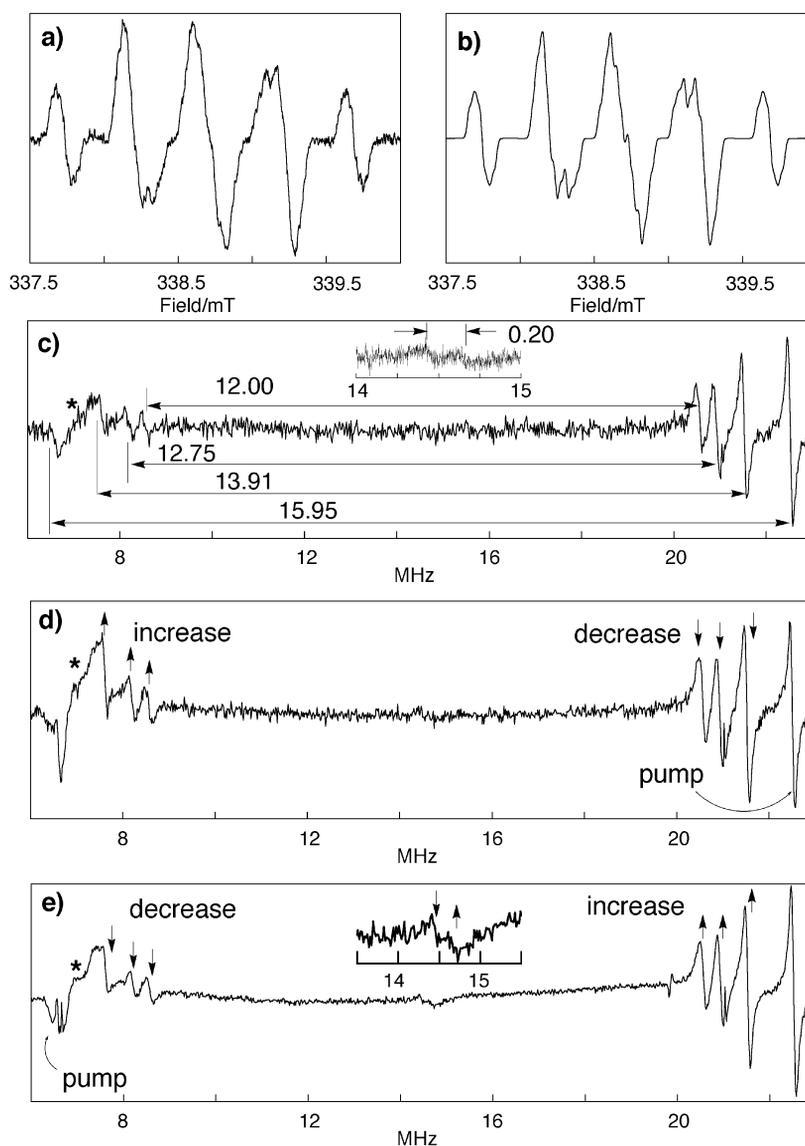


Fig. 5 (a) Hyperfine ESR (295 K, 9.515 014 0 GHz), (b) simulated, (c) ^1H -ENDOR (inset spectrum measured at 295 K), (d) ^1H -TRIPLE spectra (pump frequency, 22.54 MHz), and (e) ^1H -TRIPLE spectra (pump frequency, 6.58 MHz) observed for $(2 \text{ K}^+) \cdot 7\cdot 2^-$ generated from **7-H** with K-mirror in diglyme (1×10^{-3} M) at 305 K. The observed g -value is 2.0034. The asterisk indicates spectrometer artifacts.

Table 1 Observed and calculated proton hfccs and observed g -value for $(2\text{ K}^+)\cdot 7^{2-}$.^a

	A/mT					³⁹ K	g -value
	H(3)	H(6)	H(7)	H(9)	<i>t</i> -Bu(5)		
Obs. ^b	-0.428	-0.455	+0.496	-0.569	-0.007	$\pm 0.025^c$	2.0034
Calcd. ^d	-0.350	-0.409	-0.505	-0.568			

^aThe relative signs of the hfccs were determined by ¹H-ENDOR/TRIPLE spectroscopy.

^bThe hfccs were determined by ¹H-ENDOR spectroscopy in a diglyme solution at 305 K.

^cThis value was determined by the spectral simulation of the ESR spectrum in a diglyme solution at 295 K.

^dThese values were calculated for 3^{2-} at the UBLYP/6-31G(d, p)//UBLYP/6-31G(d, p) level of theory by *Gaussian 03* [5] with help of McConnell's equation ($Q = -2.59$ mT).

Our elaborate measurements of the ESR/¹H-ENDOR/TRIPLE spectra have afforded abundant evidence for the topological symmetry of spin density distribution of $(2\text{ K}^+)\cdot 7^{2-}$: The radical dianion possesses large spin densities on the α -carbons and two oxygen atoms similar to those of $6b^{2-}$ and 8^{2-} . These experimental results are well corroborated by the calculated results (Fig. 6). Importantly, topological symmetries of spin density distributions of the radical dianion systems show a remarkable contrast to those of neutral radical systems. Observations of these changes in topological symmetries depending on the redox states are a very rare event, and thus we termed these spin-switching natures *redox-based spin diversity* [11].

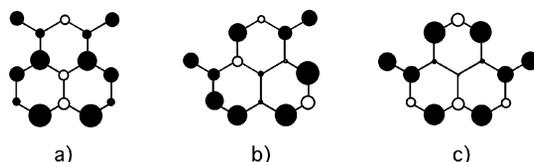


Fig. 6 Spin density distributions of (a) 2^{2-} , (b) 3^{2-} , and (c) 4^{2-} calculated at the UBLYP/6-31G(d, p)//UBLYP/6-31G(d, p) level of theory by *Gaussian 03* [5]. Filled and vacant circles denote positive and negative spin densities, respectively.

Theoretical studies on spin density distributions of 3-, 4-, and 6-oxophenalenoxyl systems

We have investigated the topological symmetries of spin density distributions of the neutral radicals and the radical dianions of 3-, 4-, and 6-oxophenalenoxyl systems in terms of resonance structures (Fig. 7) [15]. In alternant π -conjugated hydrocarbons, every other conjugated carbon atom can be starred without a direct link to each other [16]. We have applied this method to 3-, 4-, and 6-oxophenalenoxyl systems 2^\bullet , 3^\bullet , and 4^\bullet as well as the phenalenyl system **1** as an odd-alternant hydrocarbon π -radical (Fig. 7a). In the case of the phenalenyl system **1**, the α -carbon atoms can be starred. In sharp contrast in oxophenalenoxyl systems, the β -carbon and two oxygen atoms can be starred. Resonance structures of these systems point out that an unpaired electron resides at the α -positions in **1** and at both the β -positions and the two oxygen atoms in 4^\bullet , suggesting that spin densities of these systems mainly exist at the starred positions (Figs. 7a–c). Furthermore, the *redox-based spin diversity* nature also can be explained by the resonance structures. Figure 7d shows a part of resonance structures of the radical dianion 4^{2-} . Although an appreciable amount of negative charge can be delocalized on the ox-

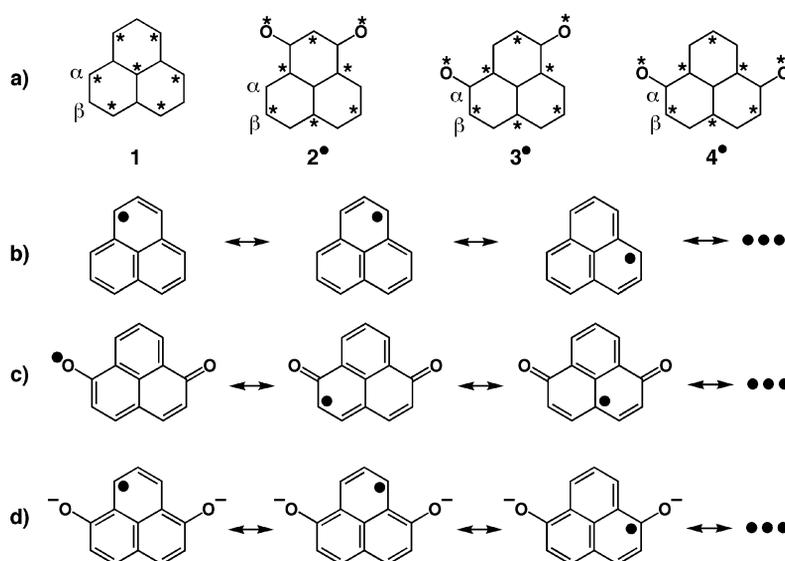


Fig. 7 (a) Molecular skeletons of **1–4•** expressed by starring carbon atoms alternately, and resonance structures of (b) **1•**, (c) **4•**, and (d) **4•²⁻**.

ophenalenoxyl skeleton, resonance structures possessing two negative charges on the two-oxygen atoms seem to provide the most important contribution to the electronic structure. These considerations consistently give us the phenalenyl-like spin delocalization nature of **4•²⁻** in sharp contrast to the neutral radical **4•**.

These discussions of resonance structures are in good agreement with the consideration based on MO pictures. Figure 8 shows MO pictures of the α -spin orbitals and MO energy diagrams of the neutral radicals **2•**, **3•**, and **4•** calculated by DFT method. In all systems, large coefficients of the SOMOs exist at the β -carbons and the two-oxygen atoms at which large spin densities of the neutral radicals appear. The coefficients of the LUMOs mostly exist at the α -carbons and the two-oxygen atoms at which

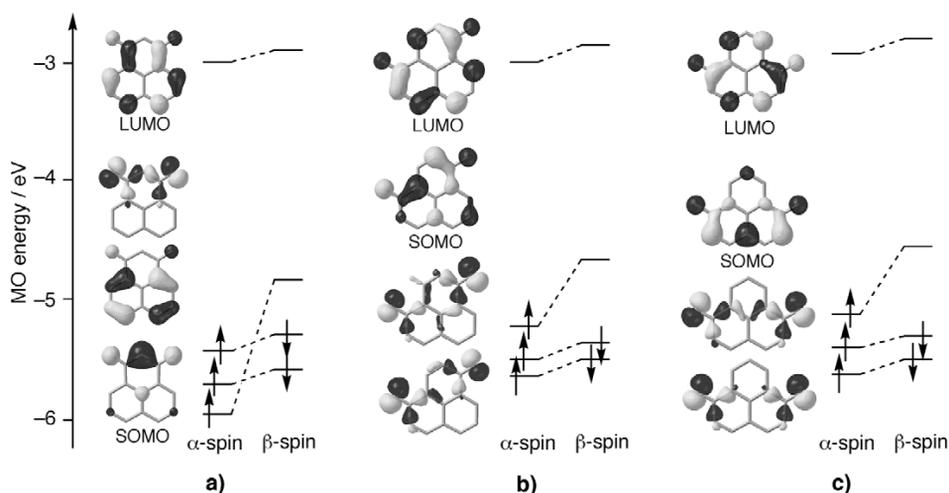


Fig. 8 MO pictures and energy diagrams of (a) **2•**, (b) **3•**, and (c) **4•** calculated at the UBLYP/6-31G(d, p)//UBLYP/6-31G(d, p) level of theory by *Gaussian 03* [5].

large spin densities of the radical dianions appear. Each LUMO energy level is almost the same value, supporting the similar reduction potentials of CV measurements. These results demonstrate that the two frontier orbitals of SOMO and LUMO play a key role in the redox abilities, causing the unique spin-delocalized natures of the oxophenalenoxyl systems.

CONCLUSION

We have for the first time designed and synthesized the oxophenalenoxyl systems as novel neutral radical systems having two oxygen atoms on the phenalenyl skeleton. These systems show an extensively spin-delocalized nature and high multi-step redox abilities like the phenalenyl system. However, the topological symmetry of spin density distributions of the oxophenalenoxyl systems is quite different from the phenalenyl system. Furthermore, each topological isomer of oxophenalenoxyls shows different topological symmetry of spin density distributions depending on the positions of the oxygen substituents, demonstrating for the first time *spin topological symmetry control* in monoradical systems.

CV studies of the anion of 3-, 4-, and 6-oxophenalenoxyl derivatives show two-step, one-electron redox abilities. The radical dianion of 4-oxophenalenoxyl derivative was first generated by K-mirror reduction of the hydroxy compound in a sealed ESR tube. ESR/¹H-ENDOR/TRIPLE studies have shown the remarkably different topological symmetry of spin density distribution of the radical dianion compared to those of the corresponding neutral radical, showing *redox-based spin diversity* nature. Such unique spin delocalization nature has been considered by taking account of topological symmetries, resonance structures, and MOs. Consequently, these studies demonstrate that the oxophenalenoxyl systems are a new class of neutral radical systems possessing markedly different spin-delocalized natures from the phenalenyl system. Furthermore, these studies demonstrate the multi-electron redox abilities and high stabilities of redox species of stable organic open-shell systems. The results provide wide applicability of stable organic open-shell systems not only for the component of new molecule-based magnetic materials but also for the *molecular crystalline secondary battery* (or *molecular spin battery*) by excess electrons [4a,11,12,17].

These unique spin-delocalized natures of oxophenalenoxyl systems will attract much attention to design and synthesize novel stable open-shell systems with an intriguing molecular functionality. Implementation of the real secondary batteries is underway.

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