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Spin Alignment in Singly Oxidized Spin-Polarized Diradical Donor: Thianthrene Bis(nitronyl nitroxide)

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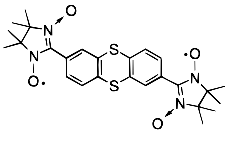
A new scientific area called “molecular magnetism” has made a rapid progress since the discovery of a ground-state quintet dicarbene by Itoh and Wasserman.[1] Recently, high-spin hyper-structured molecules have attracted considerable attention as new organic functional materials.[2] Although a topological rule for designing such high-spin molecules has been established, actual synthetic approaches of them encounter difficulties concerning generation of a number of spin-carrying centers with high kinetic stability. Under these circumstances it would be desirable to create a novel spin system with a high-spin state that can be generated by one-electron oxidation of a spin-proactive site carrying stable radical groups.[3] As a prototypical donor diradical, we prepared thianthrene derivatives carrying two nitronyl nitroxide groups (**1** and **2**). To apply this novel strategy to hyper-structured high-spin molecules, it is crucial to investigate the spin alignment in 2,7- and 2,8-isomers (**1**, **2**), especially in the singly oxidized state. *Here we found that these donor diradicals (**1**, **2**) afford ground-state quartet species upon one-electron oxidation, regardless of the substituting positions of radical groups. Interestingly, the mechanism of the spin alignment of these donor radicals in the singly oxidized state is totally different from that in the neutral state.*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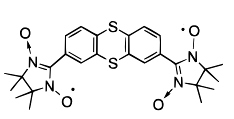
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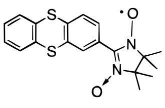
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2-Thianthrenyl nitronyl nitroxide **3** was prepared in the first place as a reference compound by an ordinary method from 2-bromothianthrene.[4] Cation diradical $3^{+\bullet}$ was generated by treating a THF solution of **3** with excess iodine. Temperature dependence of the ESR triplet signal of $3^{+\bullet}$ obeyed Curie law in the temperature range of 5−150 K,[5] suggesting that the cation diradical $3^{+\bullet}$ is a ground-state triplet species, as in cases of amine-based nitronyl nitroxides.[3c−f] Diradicals **1** and **2** were also prepared from a mixture of 2,7- and 2,8-dibromothianthrene and separated by a fractional recrystallization from chloroform. X-ray crystallographic analysis of a single crystal obtained from a more soluble fraction revealed that the specimen was 2,8-isomer **2**,[6] although the crystal structure of 2,7-isomer **1** was not determined for its poor crystallinity. Cyclic voltamograms of **1** and **2** showed two reversible redox waves at 0.95 and 1.66 V vs Ag/Ag^{+} in dichloromethane in the presence of 0.1 M Bu_4NClO_4, suggesting that stable cation diradicals can be generated reversibly. ESR spectra of both **1** and **2** in benzene solution showed nonet signals due to four equivalent nitrogen atoms with the same parameters ($a_N = 3.9$ G, and $g = 2.0062$). Before examining the magnetic behavior upon one-electron oxidation, the magnetic property of **1** and **2** in the neutral state was studied by means of a SQUID magnetometer. Temperature dependence of the paramagnetic susceptibility of these polycrystalline samples indicates that 2,7-isomer **1** exhibits a weak ferromagnetic intramolecular interaction ($J = 5.5$ K), while the intramolecular magnetic interaction of 2,8-

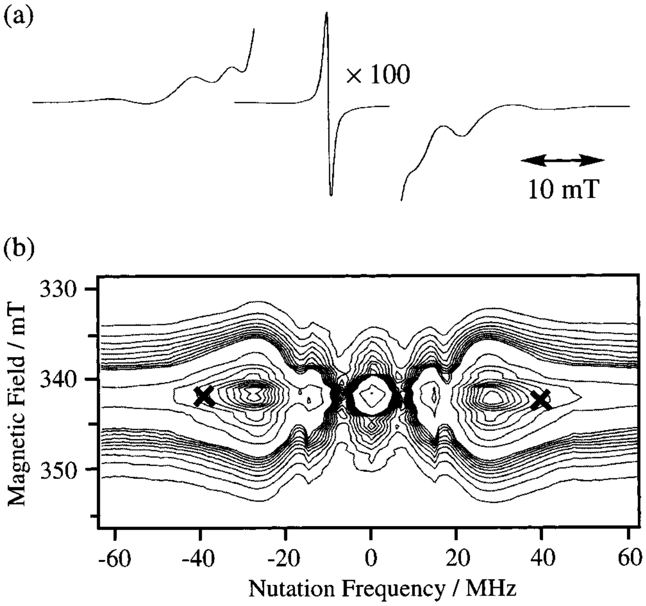

Figure 1. (a) ESR spectrum of cation triradical $1^{+\bullet}$ in a 2-methyl-THF matrix at 5 K. Fine structures of the quartet species were observed at both sides (292.7, 302.3, 308.0, 329.5, 335.3, and 344.8 mT) of the strong central signal ($g = 2.0069$) which is mainly due to unoxidized diradical **1**. (b) Contour plot of the field-swept 2D-ESTN spectra of $1^{+\bullet}$ at 5 K; ω_1 corresponds to 19.6 MHz.

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[4] Ullman, E. F.; Osiecki, J. H.; Boocock, D. G. B.; Darcy, R. *J. Am. Chem. Soc.* **1972**, *94*, 7049. An ESR spectrum of **3** in benzene solution showed a hyper-fine structure of quintet lines with $a_N = 6.2$ G and $g = 2.0062$.

[5] An ESR spectrum of the cation radical $3^{+\bullet}$, which was recorded in a frozen matrix at cryogenic temperature, showed fine structures due to the triplet species ($D = 0.0256$ cm^{-1}, $E = 0.0020$ cm^{-1}).

[6] X-ray analysis for **2**: $C_{26}H_{30}N_4O_4S_2$, fw = 526.67, *orthorhombic Pbca*, $a = 39.81(1)$ Å, $b = 18.984(5)$ Å, $c = 14.135(4)$ Å, $V = 10682(10)$ Å^3, $Z = 16$, $R_w = 0.102$, 2102 independent reflections.

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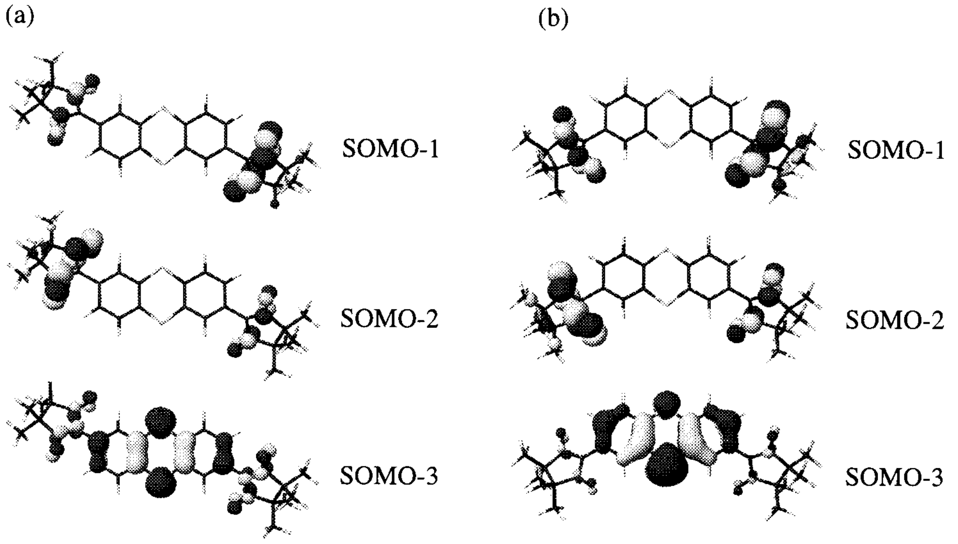
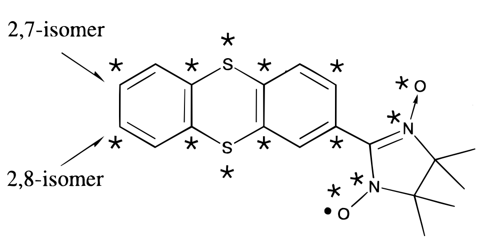


Figure 2. Three SOMOs of 2,7- and 2,8-isomer cation triradical **1**$^{+\bullet}$ (a) and **2**$^{+\bullet}$ (b). Two SOMO-3s are originated from doubly occupied MOs in neutral state of **1** and **2**.

isomer **2** is weakly antiferromagnetic ($J = -1.4$ K).[7] The magnetic coupling in these isomeric diradical donors **1** and **2** in the neutral state coincides qualitatively with the spin-polarization mechanism involving heteroatoms.[8]

The magnetic interaction in the singly oxidized state of these diradical donors **1** and **2** turned out to be in contrast with that in the neutral state. ESR spectra of cation triradicals **1**$^{+\bullet}$ and **2**$^{+\bullet}$ were also recorded in a similar condition to the case of **3**$^{+\bullet}$, along with an intense signal due to the unoxidized starting materials (see Figure 1a for **1**$^{+\bullet}$). These spectra were analyzed as due to quartet triradicals with zero-field splitting parameters of $D = 0.0125$, $E = 0.0009$ cm^{-1} for **1**$^{+\bullet}$ and $D = 0.0124$, $E = 0.0009$ cm^{-1} for **2**$^{+\bullet}$. Independent evidence for the generation of the quartet species was obtained by invoking pulsed ESR-based two-dimensional electron spin transient nutation (2D-ESTN) spectroscopy. As seen in Figure 1b, a quartet signal of **1**$^{+\bullet}$ (marked by ×) for $|M_s = \pm{}^{1}/_{2}\rangle \leftrightarrow |\mp{}^{1}/_{2}\rangle$ transition was observed at 39 MHz corresponding to $2\omega_1$ on a ridge of the intense triplet signal[9] assignable to the unoxidized radical **1** (vide supra). Although quartet transitions of $|M_s = \pm{}^{3}/_{2}\rangle \leftrightarrow |\pm{}^{1}/_{2}\rangle$ should also appear at $\sqrt{3}\omega_1$, the signal was not detected because the concentration of **1**$^{+\bullet}$ was not sufficient for giving rise to a distinct signal. Temperature dependence of quartet signals in the CW-ESR measurement obeyed Curie law in the temperature range of 5−150 K.



Theoretical calculation by PM3/UHF of **1**$^{+\bullet}$ and **2**$^{+\bullet}$ also suggests that they exist as ground-state quartet species.[10] Whereas the topological rule cannot be applied simply to cation radicals of heterocycles, the ferromagnetic coupling in the singly oxidized species **1**$^{+\bullet}$ and **2**$^{+\bullet}$ may be explained by the nondisjoint character[11] between active carbons of the thianthrene ring and the nitronyl nitroxide groups, regardless of the substitution pattern. The origin of the ferromagnetic coupling in these singly oxidized donor radicals can be rationalized more precisely by means of a molecular orbital picture.[11] Three singly occupied molecular orbitals (SOMO-1 to SOMO-3) of 2,7- and 2,8-isomer cation triradicals **1**$^{+\bullet}$ and **2**$^{+\bullet}$ are shown in Figure 2. The large ferromagnetic interactions are expected to operate between these relevant MOs, because the coefficients of SOMO-3 generated by one-electron oxidation are shared by those of SOMO-1 and SOMO-2 on the NN groups in both **1**$^{+\bullet}$ and **2**$^{+\bullet}$ species.

The mechanism of the spin alignment in this spin system can be expressed as follows: Paramagnetically interacting two unpaired electrons in the neutral species can be converted to a high-spin molecule through a ferromagnetic coupling which operates between local spins on the radical sites and a π-spin on the donor site generated upon one-electron oxidation. Although the ground-state spin multiplicity of this novel spin system is hard to predict from the simple topological rule, it can be safely rationalized by means of the space-sharing or non-space-sharing nature of nearly degenerate SOMOs. This novel spin system has the potential for constructing organic magnetic metals, nanoscale magnetic materials, and electronically controllable spin systems.

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(7) The magnetic interaction in **1** or **2** is considered to be derived not from the intermolecular origin but from the intramolecular one, since the temperature-dependent magnetic susceptibility can be fitted theoretically by using an S−T model.

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(9) The nutation frequency (27.7 MHz) of the intense signal at around 342 mT coincides with the expected value for $|S = 1, M_s = 0\rangle \leftrightarrow |1, \pm 1\rangle$ transitions of a triplet state since the value corresponds to $\sqrt{2}\omega_1$; $\omega_1 = 19.6$ MHz. Therefore, the intense peak was assigned to the triplet unoxidized diradical with a small D value. For field-swept 2D-ESTN spectroscopy applied to triplet and quartet species in nonoriented media, see: Sato, K.; Yano, M.; Furuichi, M.; Shiomi, D.; Takui, T.; Abe, K.; Itoh, K.; Higuchi, A.; Katsuma, K.; Shirota, Y., *J. Am. Chem. Soc.* **1997**, *119*, 6607−6613. Sato, K.; Shiomi, D.; Takui, T.; Itho, K.; Kaneko, T.; Tsuchida, E.; Nishide, H. *J. Spectrosc. Soc. Jpn.* **1994**, *43*, 280−291 and references therein.

(10) Although an issue of whether the ground states of **1**$^{+\bullet}$ and **2**$^{+\bullet}$ are quartets or nearly degenerate doublets still remains from the experimental side, the quartet states of them are calculated to be more stable than their doublet states by 4.6 and 4.3 kcal/mol, respectively, by a PM3/UHF method.

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