

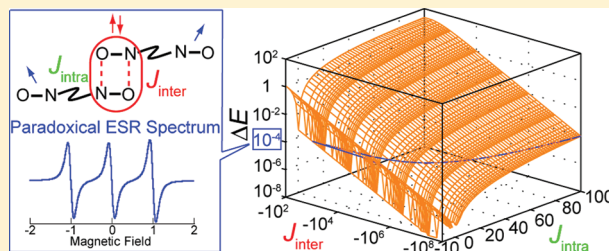
Biradical Paradox Revisited Quantitatively: A Theoretical Model for Self-Associated Biradical Molecules as Antiferromagnetically Exchange Coupled Spin Chains in Solution

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Supporting Information

ABSTRACT: An ESR hyperfine splitting pattern of a biradical in solution depends on the magnitude of the intramolecular exchange interaction J_{intra} compared with the hyperfine coupling constant A . Some biradicals exhibit their hyperfine splitting patterns characteristic of a monoradical, even though their exchange interaction is strong enough, $|J_{\text{intra}}| \gg |A|$. The contradiction in ESR spectroscopy is known as “biradical paradox”, puzzling scientists for a long time. In this study, it is shown from ESR spectral simulations underlain by a theoretical model of a series of spin Hamiltonians that noncovalent aggregation of biradical molecules in solution leads to the appearance of paradoxical ESR spectra. Most of the spins in an aggregate of one dimension lose their contribution to the ESR spectra owing to intermolecular antiferromagnetic interactions J_{inter} , leaving two outermost spins ESR-active in the aggregate of one dimension. Paradoxical ESR spectra appear only when J_{intra} and J_{inter} fall within a particular range of the magnitudes which depends on the number of molecules in the aggregate.



INTRODUCTION

Many studies have been reported on organic oligoradicals in which two or more unpaired electrons are exchange-coupled within a single molecular frame. Recent applications of oligoradicals to dynamic nuclear polarization in NMR spectroscopy or synthetic electron spin qubits for quantum information processing and quantum computers have aroused considerable interest in genuine organic biradical molecules, in which two electron spins are exchange-coupled.^{1,2} As compared to monoradicals with a single unpaired electron, exchange and dominant spin dipolar interactions are defining characteristics of organic biradicals in terms of magnetic properties: Contributions from spin–orbit interactions to the magnetic properties are less sizable.³ In quest of new functionalities underlain by these interactions, exchange interactions of biradical assemblages in solution are an important issue to be understood. In this context, we focus our attention to “biradical paradox” which has been puzzled over in chemistry.

Solution ESR spectroscopy has frequently been used to characterize electronic and spin structures of multispin systems in light of the intramolecular spin–spin exchange interactions, which are isotropic. Hyperfine structures of the ESR spectra for the organic oligoradicals are known to reflect relative magnitudes of the exchange and hyperfine interactions, which can date back to pioneering work by Weissman,⁴ Luckhurst,⁵ and Rassat.^{6,7} Restricting ourselves here to biradical molecules consisting of two stable nitroxide radical fragments, which have been thoroughly examined by focusing on the hyperfine interactions of nitroxide nitrogen nuclei, the

spin Hamiltonian is written as

$$H = H^{\text{EX}}(n = 1) + H^{\text{Z}}(n = 1) + H^{\text{HF}}(n = 1) \quad (1)$$

$$H^{\text{EX}}(n = 1) = -2J_{\text{intra}}\mathbf{S}_1 \cdot \mathbf{S}_2 \quad (2)$$

$$H^{\text{Z}}(n) = g\mu_{\text{B}}B_z \sum_{i=1}^n (S_{2i-1}^z + S_{2i}^z) \quad (3)$$

$$H^{\text{HF}}(n) = A \sum_{i=1}^n (I_{2i-1}^z S_{2i-1}^z + I_{2i}^z S_{2i}^z) \quad (4)$$

The number of biradical molecules in the present spin system is denoted by an integer $n = 1$. The redundant parameter n is, as the necessity for n described later, extended to $n > 1$, which corresponds to the 1D chain-mode aggregates of two or more biradical molecules. The first term H^{EX} represents the Heisenberg exchange interaction between the $S = 1/2$ spins in the two radical fragments with the exchange parameter J_{intra} . The second and the third terms H^{Z} and H^{HF} denote the electronic Zeeman and the hyperfine interaction for the nitrogen (^{14}N) atoms with the nuclear spin quantum number $I = 1$, respectively. The parameter A denotes the isotropic hyperfine coupling constant of the nitrogen atoms. Since H^{HF} does not commute with H^{EX} , the energy eigenvalues and the spin eigenfunctions of the total

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spin Hamiltonian, and hence the resonance field and intensity of hyperfine ESR transitions, depend on the relative magnitudes of $|J_{\text{intra}}|$ and $|A|$. As described in the literature,^{4–10} the extreme limit of $|J_{\text{intra}}| \gg |A|$ or $|J_{\text{intra}}| \ll |A|$ gives simple hyperfine splitting patterns in ESR spectra reflecting the relative magnitudes. Biradicals in the weak exchange limit of $|J_{\text{intra}}| \ll |A|$ exhibit the hyperfine splitting pattern with a spacing of $|A|$ characteristic of half the molecule, i.e., the corresponding monoradical. On the other hand, when the exchange interaction $|J_{\text{intra}}|$ is much larger than the hyperfine interaction $|A|$ (the strong exchange limit), the hyperfine splitting pattern consists of nearly doubled number of lines with the spacing of $|A|/2$. Intermediate cases of $|J_{\text{intra}}| \sim |A|$ give rise to complicated hyperfine splitting patterns. The magnitude of hyperfine interaction $|A|$ falls within the order of 10^1 Oe (1 mK or 10^{-3} cm⁻¹ for $g = 2$) for the nitrogen nuclei in stable nitroxide radicals. It is feasible to determine the magnitude of exchange interaction $|J_{\text{intra}}|$ in this range of energy from the hyperfine splitting pattern. Thus, the hyperfine splitting patterns have been a spectroscopic “probe” for intramolecular exchange interactions in metal-containing proteins, spin-labeled biomolecules,^{11–13} and stable nitroxide oligoradicals as building blocks for crystalline magnetic materials.^{14,15}

ESR spectra from some biradicals in solution show hyperfine splitting patterns of their corresponding monoradicals which are characteristic of the weak exchange limit of $|J_{\text{intra}}| \ll |A|$, although their exchange interaction $|J_{\text{intra}}|$ seems strong enough ($|J_{\text{intra}}| \gg |A|$). The occurrence of such ESR spectra as displaying contradictory features of hyperfine splittings have been known as “biradical paradox”.¹⁰ The history of the biradical paradox has been initiated by Chichibabin’s hydrocarbon.^{4,16–18} A mechanism giving the paradoxical monoradical-like spectra has been proposed for Chichibabin’s hydrocarbon: two molecules should form a covalent bond at the radical sites, quenching two unpaired electron spins, while the covalent bond formation leaves two uncoupled spins in the resultant oligomeric biradical. The uncoupled spins behave as monoradicals.^{19,20} As for the ground electronic and spin state of Chichibabin’s hydrocarbon, however, the inconsistencies of conflicting experimental observations^{10,21,22} including those on single crystals²³ remain unsolved. This would be related to paramagnetic impurities resulting from the high reactivity, or chemical instability, of Chichibabin’s hydrocarbon in solution.

The biradical paradox has been found as well in chemically stable biradicals with low reactivity. Stable nitroxide biradicals based on diazaadamantane²⁴ and dithiazole biradicals^{25,26} having a strong intramolecular exchange interaction J_{intra} ($|J_{\text{intra}}| \gg A$) have been shown to exhibit paradoxical monoradical-like hyperfine splitting patterns. As a mechanism for the paradox of the stable biradicals, noncovalent association in fluid solutions has been proposed.^{24–26} Two or more biradical molecules can be noncovalently associated to form dimers or larger aggregates. Unpaired electron spins except two outermost spins on the periphery of the aggregate should lose their contribution to the ESR spectra when strong antiferromagnetic interactions occur at the association sites of the neighboring molecules in the aggregate. The outermost spins are spatially and magnetically separated far enough to render exchange interactions between them very weak, giving paradoxical monoradical-like ESR signals attributed to the outermost spins.^{24–26}

In this paper, we revisit the model of the noncovalent self-association^{24–26} for solving the biradical paradox especially for nitroxide radical derivatives. In our theoretical model, we have taken great care over the magnitude of the intermolecular exchange interaction J_{inter} operating at the association sites in

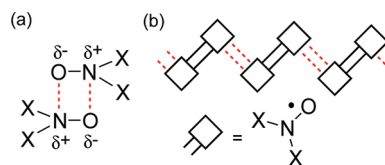


Figure 1. (a) Noncovalent self-association of nitroxide radicals driven by charge polarizations. (b) Schematic view of the oligomeric self-association of biradical molecules. The squares represent the N–O radical fragments of the biradical molecules. The dotted lines denote the Coulombic interaction giving the four-centered binding of the N–O groups. The binding results in the intermolecular antiferromagnetic exchange interactions.

the aggregate as compared with the intramolecular exchange interaction J_{intra} and the thermal energy $k_{\text{B}}T$. The key feature of the model is the two outermost spins interacting weakly with each other. This interpretation leads to the fact that the $2n$ -spin system of the n -meric aggregate should be equivalent to an effective two-spin system. In the present elaborate study, the intuitive model of the equivalence is rationalized by calculating spin–spin correlation functions and ESR spectral simulation based on a model spin Hamiltonian. From the calculations, it is shown that the effective exchange interaction J_{eff} between the outermost spins is sufficiently suppressed to afford paradoxical monoradical-like ESR spectra only when the genuine intra- and intermolecular exchange interactions J_{inter} and J_{intra} of the biradical fall within some particular range of the magnitudes of the exchange interactions. The previous studies based on the qualitative or intuitive hypothesis of the molecular association^{24–26} cannot afford insights into quantitative understanding of the paradox, having overlooked such consistency with the magnitudes of the genuine exchange interactions. In fact, we are not allowed to find realistic magnitudes of the exchange interactions J_{inter} and J_{intra} giving the paradoxical monoradical-like ESR spectra in the framework of the four-spin model of dimerized biradical molecules ($n = 2$). Multimolecular aggregation of more than five biradical molecules can afford to give the consistency of the magnitudes of the exchange interactions.

RESULTS AND DISCUSSION

A Spin Model Representing Molecular Aggregation. Some of neutral nitroxide monoradicals are known to make noncovalently bound dimers in solutions.²⁷ The self-association of the electrically neutral radical molecules is brought about by a partial charge polarization of the nitroxide group, $\text{N}^{\delta+}-\text{O}^{\delta-}$, which provides possible four-centered binding of the nitroxide groups,^{24a} as shown in Figure 1. The partial charge polarization of the N–O group gives attractive forces for the self-association. A nitroxide biradical molecule has two binding sites of the N–O groups, leading to oligomeric self-association of $n \geq 2$ molecules, as illustrated in Figure 1. The association at the N–O groups is known to give intermolecular exchange interactions J_{inter} .^{27c,28,29} Particularly, the four-centered binding of the N–O groups provides a very strong antiferromagnetic interaction in the order of $|J_{\text{inter}}|/k_{\text{B}} \sim 10^3$ K.^{27c,28–31} On the other hand, the magnitude of the intramolecular exchange interaction J_{intra} strongly depends on molecular geometry around the N–O groups, which provides a plausible range of J_{intra} in the order of $|J_{\text{intra}}|/k_{\text{B}} = 10^0\text{--}10^2$ K.^{24a,32–34} Thus, the spin system of the oligomeric aggregate of the self-associated n -mer is represented by

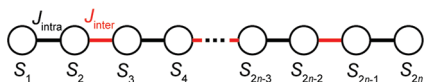


Figure 2. Schematic diagram of the spin Hamiltonian for the $2n$ -spin system of the self-associated n biradicals. The circles show the $S = 1/2$ spins. The black lines represent the intramolecular exchange interaction J_{intra} while the red lines the intermolecular exchange interaction J_{inter} .

the Heisenberg spin Hamiltonian

$$H^{\text{EX}}(n \geq 2) = -2J_{\text{intra}}\mathbf{S}_1 \cdot \mathbf{S}_2 + \sum_{i=2}^n (-2J_{\text{inter}}\mathbf{S}_{2i-2} \cdot \mathbf{S}_{2i-1} - 2J_{\text{intra}}\mathbf{S}_{2i-1} \cdot \mathbf{S}_{2i}) \quad (5)$$

where n represents the number of biradicals constructing the $2n$ -spin system, as illustrated in Figure 2.³⁵ The intramolecular exchange interaction in the biradical is denoted by J_{intra} between S_{2i-1} and S_{2i} , while the intermolecular interaction J_{inter} results from the four-centered binding of the N–O groups.

When a very strong antiferromagnetic interaction J_{inter} occurs between S_{2i-2} and S_{2i-1} , most of the spins in the $2n$ -spin system should lose contribution to ESR spectra except for two outermost spins S_1 and S_{2n} . Thus, the $2n$ -spin system should be regarded as an effective two-spin system. The self-associated aggregate of n molecules is approximated by the two-spin system

$$H_{\text{eff}}^{\text{EX}}(n \geq 2) = -2J_{\text{eff}}\mathbf{S}_1 \cdot \mathbf{S}_{2n} \quad (6)$$

where J_{eff} denotes the effective exchange interaction between the outermost spins. The equivalence between the $2n$ -spin system of the n -meric aggregate and the effective two-spin system with J_{eff} is rationalized below by calculating spin–spin correlation functions and ESR spectral simulation based on the spin Hamiltonians. After the equivalence is established, the condition of J_{intra} and J_{inter} is discussed in which the magnitude of $|J_{\text{eff}}|$ falls within the weak-exchange limit of $|J_{\text{eff}}| \ll |A|$, giving a monoradical-like ESR spectrum.

Reduction of a Four-Spin System ($n = 2$) to an Effective Two-Spin System. As described above, most of the spins in the linear chain system of eq 5 (Figure 2) lose their contribution to ESR spectra except for the two outermost spins, when the intermolecular antiferromagnetic interactions are very strong. The $2n$ -spin system of n biradical molecules is equivalent to an effective two-spin system. This physical picture is intuitive, but can be rationalized by calculating a model spin Hamiltonian. At first, a minimal system of two biradical molecules, i.e., a dimer of biradicals, is examined for simplicity, whose spin Hamiltonian is given as follows:

$$H^{\text{EX}}(n = 2) = -2J_{\text{intra}}\mathbf{S}_1 \cdot \mathbf{S}_2 - 2J_{\text{inter}}\mathbf{S}_2 \cdot \mathbf{S}_3 - 2J_{\text{intra}}\mathbf{S}_3 \cdot \mathbf{S}_4 \quad (7)$$

The exchange-coupled system composed of four $S = 1/2$ spins has six eigenstates (spin-multiplets); two singlet ($S = 0$) states (S_A, S_B), three triplet ($S = 1$) states (T_A, T_B, T_C), and a quintet ($S = 2$) state (Q). The energy level diagrams of the states calculated by diagonalization³⁶ of eq 7 are shown in Figure 3 as a function of $|J_{\text{inter}}/J_{\text{intra}}|$ for both positive and negative values of J_{intra} . As the intermolecular antiferromagnetic interaction $|J_{\text{inter}}|$ increases with respect to $|J_{\text{intra}}|$, the singlet ground state (S_A) and the first excited triplet state (T_A) are stabilized, as shown in Figure 3. For the plausible range of $|J_{\text{intra}}|/k_B = 10^0 - 10^2$ K and $J_{\text{inter}}/k_B \sim -10^3$ K, as known from the literatures,^{27c,28–34} the energy gap ΔE_{2-1} between the first excited state and the second excited state

$$\Delta E_{2-1} = \begin{cases} E(Q) - E(T_A) & (J_{\text{intra}} > 0) \\ E(S_B) - E(T_A) & (J_{\text{intra}} < 0) \end{cases} \quad (8)$$

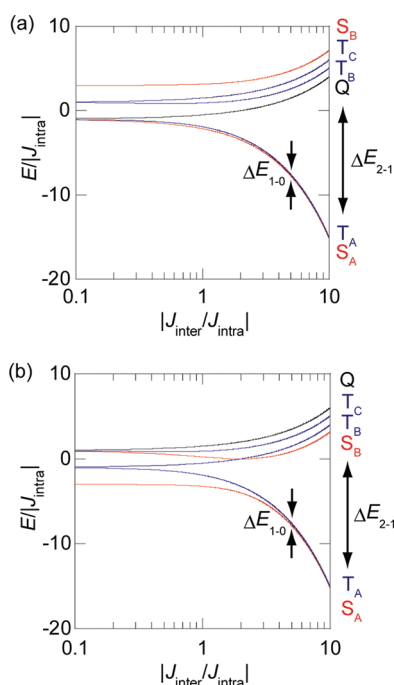


Figure 3. Energy diagrams for the four-spin system as a function of the interaction ratio $J_{\text{inter}}/J_{\text{intra}}$ (a, $J_{\text{intra}} > 0$; b, $J_{\text{intra}} < 0$). The symbols Q, T, and S stand for the quintet ($S = 2$), triplet ($S = 1$) and singlet ($S = 0$) state, respectively. The energy gap between the ground state and the first excited state is denoted by ΔE_{1-0} , while that between the first and the second excited states by ΔE_{2-1} .

is found to be $\Delta E_{2-1}/k_B \sim 2 \times 10^3$ K,³⁷ which gives little thermal population of the second excited (Q or S_B) and higher states (T_B, T_C and S_B or T_B, T_C , and Q). The larger $|J_{\text{inter}}|$ gives the larger ΔE_{2-1} . Therefore, ESR experiments are involved only with the low-lying S_A and T_A states when the interactions are $|J_{\text{intra}}|/k_B \sim 10^0 - 10^2$ K and $J_{\text{inter}}/k_B \geq -10^3$ K, or $|J_{\text{inter}}/J_{\text{intra}}| \geq 10$.

From the energy level calculations, it has been found that the exchange-coupled system of four $S = 1/2$ spins are described only by the low-lying S_A and T_A states, when the relative magnitude of the exchange interactions J_{inter} and J_{intra} is in a particular range as found in real biradical compounds. Now, an important issue to be solved is whether the low-lying S_A and T_A states are described only by the outermost spins, S_1 and S_4 , in the four-spin system. The nature of the low-lying states is examined from spin–spin correlation functions. The correlation functions for a spin pair of S_j and S_k ($j, k = 1, 2, 3, 4$) is calculated from the spin eigenfunction, which are defined as the expectation value $\langle S_j \cdot S_k \rangle$ for the S_A and T_A states. In general, for an exchange-coupled pair of two $S = 1/2$ spins, S_I and S_{II} , the triplet state has a correlation of $\langle S_I \cdot S_{II} \rangle = +1/4$, while the singlet state has $\langle S_I \cdot S_{II} \rangle = -3/4$. If the two outermost spins, S_1 and S_4 , in the four-spin system have these values of the correlation function in an eigenstate, the eigenstate is equivalent to the triplet or singlet state of the genuine two-spin system and thus the four-spin system can be approximated by the effective two-spin system composed only of the two outer spins, S_1 and S_4 . The calculated correlation functions are shown in Figure 4 as a function of the ratio $|J_{\text{inter}}/J_{\text{intra}}|$. Both for $J_{\text{intra}} > 0$ and $J_{\text{intra}} < 0$, the correlation $\langle S_1 \cdot S_4 \rangle$ between the two outermost spins approaches $+1/4$ or $-3/4$ for T_A and S_A states in the limit of $|J_{\text{inter}}/J_{\text{intra}}| \gg 1$. This means that

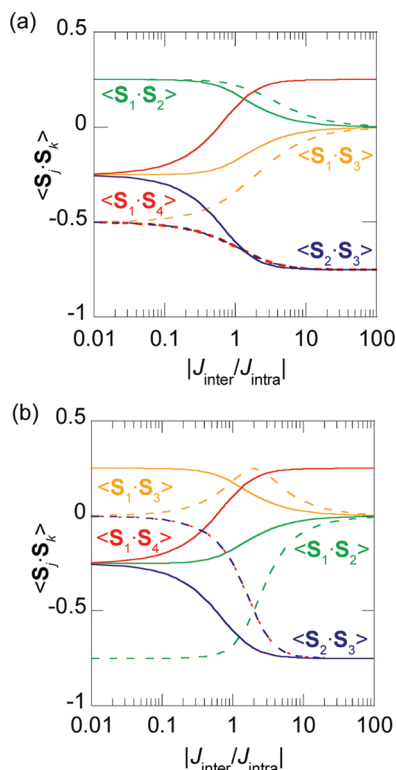


Figure 4. Spin–spin correlation functions calculated for the four-spin system as a function of the interaction ratio $|J_{\text{inter}}/J_{\text{intra}}|$ (a, $J_{\text{intra}} > 0$; b, $J_{\text{intra}} < 0$). The green, orange, red, and blue lines denote the spin–spin correlation function $\langle S_1 \cdot S_2 \rangle$, $\langle S_1 \cdot S_3 \rangle$, $\langle S_1 \cdot S_4 \rangle$, and $\langle S_2 \cdot S_3 \rangle$, respectively. The solid and dashed lines denote the correlation in the lowest triplet (T_A) and the singlet (S_A) eigenstates, respectively.

the two remote spins, S_1 and S_4 , make a triplet or singlet state in the low-lying T_A and S_A states, respectively, for $J_{\text{intra}} > 0$ and $J_{\text{intra}} < 0$. The correlations between one of the two outer spins S_1 and the inner spins S_2 and S_3 , $\langle S_1 \cdot S_2 \rangle$ and $\langle S_1 \cdot S_3 \rangle$, are zero in the limit of $|J_{\text{inter}}/J_{\text{intra}}| \gg 1$ and, furthermore, the inner spins, S_2 and S_3 , have the correlation expected for a spin pair in a singlet state, $\langle S_2 \cdot S_3 \rangle = -3/4$. These indicate that the inner spins, S_2 and S_3 , have no contribution to the resultant spin structure of the S_A and T_A state in the limit of $|J_{\text{inter}}/J_{\text{intra}}| \gg 1$. It is concluded from these calculations that the four-spin system can be equivalent to the effective two-spin system composed only of the two outer spins. Only the outer spins S_1 and S_4 should be detectable in ESR spectroscopy in the limit of $|J_{\text{inter}}/J_{\text{intra}}| \gg 1$.

Requirements for the Appearance of the Paradoxical ESR Spectra. The condition for the appearance of paradoxical ESR spectra is examined in light of the effective two-spin system, to which the four-spin system of the biradical dimer has been found to be equivalent, as shown above. The energy gap between the low-lying triplet (T_A) and the singlet (S_A) states in the four-spin system

$$\Delta E_{1-0} \equiv E(T_A) - E(S_A) \quad (9)$$

governs the ESR spectra when the two states are separated from excited states by the large energy gap ΔE_{2-1} . The gap ΔE_{1-0} strongly depends on J_{intra} and J_{inter} values, as shown in Figure 5. It is likely that we are allowed to set the energy gap ΔE_{1-0} of the four-spin system equal to the effective singlet–triplet energy

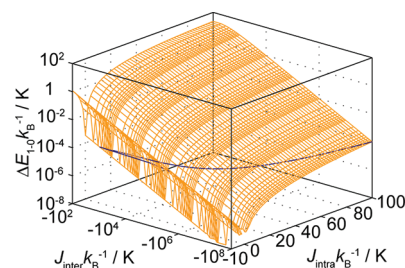


Figure 5. Energy gap ΔE_{1-0} between the ground and the first excited states in the four-spin system of eq 7 as a function of the intramolecular interaction J_{intra} and the intermolecular interaction J_{inter} . The blue line denotes the trajectory of $\Delta E_{1-0}/k_B = 10^{-4}$ K.

gap $2J_{\text{eff}}$

$$2J_{\text{eff}} = \Delta E_{1-0} \quad (10)$$

of the effective two-spin system of S_1 and S_4 . The energy equivalence of eq 10 is verified by simulating ESR spectra by use of both the four-spin Hamiltonian

$$H = H^{\text{EX}}(n=2) + H^Z(n=2) + H^{\text{HF}}(n=2) \quad (11)$$

and the effective two-spin Hamiltonian

$$H = H_{\text{eff}}^{\text{EX}}(n=2) + g\mu_B B_z(S_1^z + S_4^z) + A(I_1^z S_1^z + I_4^z S_4^z) \quad (12)$$

The ESR spectra simulated for the dimer of biradicals based on the four-spin model of eq 11 are illustrated in Figure 6a.³⁸ In the simulations, the intramolecular exchange interaction and the hyperfine coupling constant are fixed as $J_{\text{intra}}/k_B = 10$ K and $A/g\mu_B = 1.5$ mT with changing the intermolecular exchange interaction J_{inter} .³⁹ When J_{inter} is comparable to J_{intra} , $|J_{\text{inter}}|/k_B = 1$ – 10 K ($|J_{\text{inter}}/J_{\text{intra}}| = 0.1$ – 1), the spectrum exhibits equally separated nine lines, which is characteristic of nitroxide tetraradicals.⁴⁰ When J_{inter} values become larger than J_{intra} , $|J_{\text{inter}}|/k_B \sim 10^3$ K ($|J_{\text{inter}}/J_{\text{intra}}| \sim 10^2$), five-line splitting patterns appear as expected for nitroxide biradicals.⁴¹ This is consistent with the discussion based on the spin–spin correlation function described above. The two inner spins lose their contribution to ESR spectra and the two outer spins behave like a biradical. The gap ΔE_{1-0} is calculated from eq 7. The interaction $|J_{\text{inter}}|/k_B = 10^3$ K ($|J_{\text{inter}}/J_{\text{intra}}| = 10^2$) gives $\Delta E_{1-0}/k_B = 9.9 \times 10^{-2}$ K from eq 7. The two-spin Hamiltonian (eq 12) with $2J_{\text{eff}}/k_B = 9.9 \times 10^{-2}$ K yields a five-line spectrum as shown in Figure 6b. The spectral feature is the same as that for $\Delta E_{1-0}/k_B = 9.9 \times 10^{-2}$ K from $|J_{\text{inter}}/J_{\text{intra}}| = 10^3/10$ in Figure 6a. On increasing $|J_{\text{inter}}|$ or $|J_{\text{inter}}/J_{\text{intra}}|$, the biradical-like five-line spectrum changes into a monoradical-like three-line spectrum for $|J_{\text{inter}}|/k_B \sim 10^6$ K ($|J_{\text{inter}}/J_{\text{intra}}| \sim 10^5$). The parameters $|J_{\text{inter}}/J_{\text{intra}}| = 10^4/10$, $10^5/10$, and $10^6/10$ give $\Delta E_{1-0}/k_B = 1.0 \times 10^{-2}$ K, 1.0×10^{-3} K and 1.0×10^{-4} K, respectively (Figure 5). With setting $2J_{\text{eff}}$ equal to these ΔE_{1-0} values, the two-spin Hamiltonian (eq 12) reproduces the spectral feature of the four-spin system, as depicted in Figure 6, a and b. Thus, the energy equivalence of eq 10 has been verified by the ESR spectral simulation. The dimer of biradicals can afford a biradical-like ESR spectrum for a large intermolecular exchange interaction J_{inter} in the order of $|J_{\text{inter}}|/k_B \sim 10^3$ K or $|J_{\text{inter}}/J_{\text{intra}}| \sim 10^2$, which corresponds to $\Delta E_{1-0}/k_B = 2J_{\text{eff}}/k_B \sim 9.9 \times 10^{-2}$ K. Even a monoradical-like spectrum, as expected for the biradical paradox, can appear in the case of quite a large interaction in the order of $|J_{\text{inter}}|/k_B > 10^6$ K or

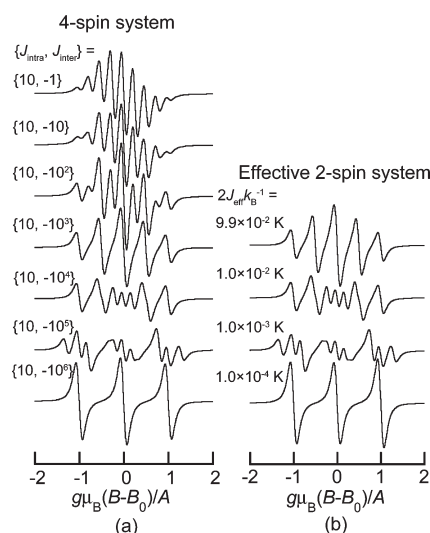


Figure 6. (a) Simulated ESR spectra on the basis of the four-spin system (eq 11) (a) and the effective two-spin system (eq 12) (b). The parameters used in the simulation are $g = 2.0$, $A/g\mu_B = 1.5$ mT, and $\nu = 9.23752$ GHz. The horizontal axis represents the reduced magnetic field normalized by A , $g\mu_B(B - B_0)/A$, where the central field is defined as $B_0 = h\nu/g\mu_B$. In the simulation of the four-spin system (a), the exchange interaction parameters are set as $\{J_{\text{intra}}, J_{\text{inter}}\} = \{10, -10^3\}$, $\{10, -10^4\}$, $\{10, -10^5\}$, and $\{10, -10^6\}$. These exchange parameters have been found to give $\Delta E_{1-0}/k_B = 9.9 \times 10^{-2}$ K, 1.0×10^{-2} , 1.0×10^{-3} , and 1.0×10^{-4} K. With setting the parameter $2J_{\text{eff}}$ equal to these ΔE_{1-0} values, the simulation with the two-spin Hamiltonian has been given as depicted in (b).

$|J_{\text{inter}}/J_{\text{intra}}| > 10^5$, corresponding to $\Delta E_{1-0}/k_B = 2J_{\text{eff}}/k_B < 10^{-4}$ K.

Now, the range of magnitudes for J_{inter} and J_{intra} giving $\Delta E_{1-0}/k_B = 2J_{\text{eff}}/k_B < 10^{-4}$ K, which corresponds to the paradoxical ESR spectra, is examined. The trajectory, the locus, of points $\{J_{\text{intra}}, J_{\text{inter}}\}$ giving $\Delta E_{1-0}/k_B = 10^{-4}$ K is shown in Figure 5 and its projection onto the $\{J_{\text{intra}}, J_{\text{inter}}\}$ plane is depicted in Figure 7. The lower area of $\{J_{\text{intra}}, J_{\text{inter}}\}$ bounded by the trajectory corresponds to $\Delta E_{1-0}/k_B = 2J_{\text{eff}}/k_B < 10^{-4}$ K, and thus, gives the paradoxical ESR spectra for the dimer of biradical molecules ($n = 2$). When J_{intra} is assumed to fall within a realistic magnitude, $J_{\text{intra}}/k_B \sim +10$ K,^{24a,32–34} the criterion $\Delta E_{1-0}/k_B = 2J_{\text{eff}}/k_B < 10^{-4}$ K is fulfilled only by an unrealistically large magnitude of the intermolecular antiferromagnetic interaction $J_{\text{inter}}/k_B > 10^6$ K. For a probable order of magnitude of $|J_{\text{inter}}|/k_B < 10^3$ K,^{27c,28,29} in turn, $\Delta E_{1-0}/k_B = 2J_{\text{eff}}/k_B < 10^{-4}$ K is given only in a narrow area of $|J_{\text{intra}}|/k_B < 0.3$ K, as depicted by the line for $n = 2$ in Figure 7.

The association of two biradical molecules brings about peripheral spins which are weakly coupled by effective exchange interactions. The calculations described above indicate that the effective interaction giving paradoxical ESR spectra is given only when the intra- and intermolecular exchange interactions fall within some particular range of magnitudes. The previous studies have proposed qualitative or intuitive hypothesis of the molecular association, or dimerization, as a solution to the ESR paradox.^{24–26} They have, however, overlooked the consistency with magnitudes of the intra- and intermolecular exchange interactions.

Oligomeric Association of More than Two Molecules. It has been found from the calculations of the correlation functions that

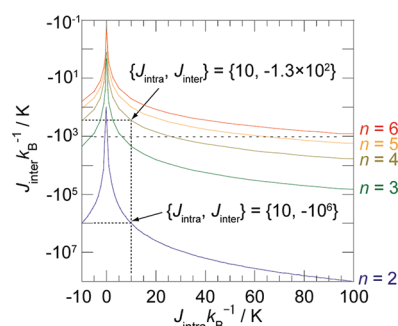


Figure 7. Calculated trajectory of points $\{J_{\text{intra}}, J_{\text{inter}}\}$ giving $\Delta E_{1-0}/k_B = 10^{-4}$ K in the $2n$ -spin model (eq 7 for $n = 2$ and eq 5 for $3 \leq n \leq 6$). The lower area of $\{J_{\text{intra}}, J_{\text{inter}}\}$ bounded by the trajectory corresponds to $\Delta E_{1-0}/k_B < 10^{-4}$ K, giving the paradoxical monoradical-like ESR spectra.

the four-spin system of the biradical dimer ($n = 2$) can be approximated by the effective two-spin system composed of the two outer spins. Only the outermost spins are detectable in ESR in the limit of $|J_{\text{inter}}/J_{\text{intra}}| \gg 1$. The same conclusion is obtained for larger aggregates of a trimer ($n = 3$), a tetramer ($n = 4$), a pentamer ($n = 5$), and a hexamer ($n = 6$).⁴² In the limit of $|J_{\text{inter}}/J_{\text{intra}}| \gg 1$, the lowest-lying singlet and triplet states are found to be separated from excited states by a large energy gap ΔE_{2-1} in the energy spectra of the eigenstates (spin multiplets) for the spin Hamiltonian (eq 5). The correlation functions indicate that the $2n$ -spin systems are approximated by the effective two-spin system composed only of the two outermost spins, S_1 and S_{2n} , corresponding to the lowest-lying singlet and triplet states. Thus, we are allowed to approximate the larger aggregates as an effective two-spin system as well as the minimal aggregate as the biradical dimer. It should be noted that the energy gap ΔE_{2-1} between the first excited state (T_A) and the second excited state (a quintet or a singlet state) is found to be little affected by the system size n ; the aggregates with $n = 2, 3, 4, 5$, and 6 have $\Delta E_{2-1}/k_B = 2.0 \times 10^3$ K for $\{J_{\text{intra}}/k_B, |J_{\text{inter}}|/k_B\} = \{10, 10^3\}$ and $\Delta E_{2-1}/k_B = 1.9 \times 10^2$ K for $\{J_{\text{intra}}/k_B, |J_{\text{inter}}|/k_B\} = \{10^2, 10^3\}$.⁴³

The energy gap ΔE_{1-0} between the low-lying singlet and triplet states for the $2n$ -spin system of $n \geq 3$ is regarded as the singlet–triplet gap $2J_{\text{eff}}$ for the effective two-spin system, as found in the dimeric four-spin system. The range of magnitudes for J_{inter} and J_{intra} , which gives paradoxical ESR spectra corresponding to $\Delta E_{1-0}/k_B = 2J_{\text{eff}}/k_B < 10^{-4}$ K, is examined for the larger aggregates of $n \geq 3$. The trajectory of points $\{J_{\text{intra}}, J_{\text{inter}}\}$ giving $\Delta E_{1-0}/k_B = 10^{-4}$ K for $n \geq 3$ calculated with eq 5 is compared with that for $n = 2$ in Figure 7. The lower area of $\{J_{\text{intra}}, J_{\text{inter}}\}$ bounded by the trajectory gives $\Delta E_{1-0}/k_B = 2J_{\text{eff}}/k_B < 10^{-4}$ K and the paradoxical ESR spectra for $n \geq 3$. We find that for a fixed value of J_{intra} , the threshold of J_{inter} giving the criterion $2J_{\text{eff}}/k_B < 10^{-4}$ K decreases as n increases. For $J_{\text{intra}}/k_B = 10$ K, for example, $|J_{\text{inter}}|/k_B$ should be unrealistically larger than 10^6 K in the $n = 2$ system, while $|J_{\text{inter}}|/k_B > 1.3 \times 10^2$ K gives the criterion $2J_{\text{eff}}/k_B < 10^{-4}$ K for $n = 4$. For a plausible magnitude of $J_{\text{intra}}/k_B = 10^2$ K, an acceptable magnitude of $|J_{\text{inter}}|/k_B \sim 10^3$ K is allowed to give paradoxical ESR spectra ($2J_{\text{eff}}/k_B < 10^{-4}$ K) when the aggregate has the larger size of $n = 6$. It is found from the calculations that the threshold of the intermolecular antiferromagnetic interaction J_{inter} giving paradoxical ESR spectra decreases when the formation of self-associated molecular aggregates occurs. The consistency with magnitudes of the plausible

intra- and intermolecular exchange interactions, which has been overlooked in the previous studies, is thus recovered by the multimolecular aggregation.

CONCLUSION

There has been intuitive interpretation of the biradical paradox assuming the noncovalent self-association of biradical molecules, which gives magnetically free spins in the periphery of the molecular aggregate. We have revisited the paradox to disclose the most insightful physical characteristics of the appearance of paradoxical solution ESR in a quantitative manner. We emphasize that this work has treated the paradox in quantum-mechanical terms and disclosed what the previous reports overlooked. We have first rationalized the generation of the weakly coupled spins in the noncovalently bound aggregate by calculating the spin Hamiltonian mimicking the aggregate of one dimension. The further theoretical treatment of the spin Hamiltonian with varying the size of the aggregates has shown that the effective exchange interaction between the peripheral spins is in the weak-exchange limit giving the paradoxical ESR spectra in solution, when the genuine intra- and intermolecular exchange interactions of the biradical fall within some particular range of their magnitudes. In fact, it is not until the aggregation exceeds more than five molecules that the paradoxical ESR spectra for ordinary nitroxide biradicals with realistic interactions $\{J_{\text{intra}}J_{\text{inter}}\}$ occur.⁴⁴ The consistency with the magnitudes of the exchange interactions giving the paradoxical spectra, which depends on the aggregation number, has been overlooked by the previous studies of qualitative or intuitive hypothesis of the molecular association. The present theoretical study gives a generalized solution to the long-standing problem of the biradical paradox.

ASSOCIATED CONTENT

S Supporting Information. Calculations of the spin Hamiltonian; ESR spectral simulations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(39) Simulated ESR spectra calculated on the basis of the four-spin system (eq 11) with other combinations of $\{J_{\text{intra}}, J_{\text{inter}}\}$ are given in Figure S7 of the Supporting Information. The array $\{J_{\text{intra}}/k_B, |J_{\text{inter}}|/k_B\}$ has been set to be ranging $\{-10$ to $+100, 1$ to $10^7\}$.

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(43) The energy gap ΔE_{2-1} calculated for $n \geq 3$ from eq 5 is given in Figure S8 of Supporting Information.

(44) A critical piece of evidence for the experimental detectability of the oligomeric aggregates has been obtained from ESI (electrospray ionization) mass spectrometry for a nitroxide biradical,^{44a} which is shown to exhibit paradoxical monoradical-like ESR spectra in solutions. The ESI-MS consists of a series of mass peaks assignable to aggregates containing pentamers ($n = 5$). There should exist the distribution of the aggregates whose size is governed by the association equilibrium in a solution. Our experimental ESR spectra consist of the paradoxical monoradical-like signals from the large aggregates and an additional broad signal. The broad spectrum is assigned to the smaller aggregates such as dimers and trimers. The total intensity, or spin susceptibility, of the ESR spectra is found to be reduced as compared with that expected for the concentration of the biradical, which is consistent with the antiferromagnetic spin pairing within the molecular aggregate. Analyses of these experimental results are underway in terms of the association equilibrium and the results will be published elsewhere. (a) Kanzaki, Y.; Shiomi, D.; Sawai, T.; Sato, K.; Okada, K.; Takui, T. Presented at the 12th International Conference on Molecule-Based Magnets, Beijing, China, October 8–12, 2010.