Novel Photo-excited Triplet State Arising from Four Unpaired Electrons: π-Topology and Spin Alignment in Excited State of Organic Spin System

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A novel photo-excited state with the intermediate spin ($S = 1$) arising from four unpaired spins and a nearly degenerate quintet ($S = 2$) excited state were detected for **1**, which was designed utilizing the photo-excited triplet spin coupler by taking π-topology into account. The unique triplet state has an interesting electronic structure, which D value is reduced by the antiferromagnetic spin alignment between two radical spins through the excited spin coupler.

The spin manipulation is a very challenging topic in the field of the molecular magnetism. The π-topology plays an important key role in the spin manipulation as well as the molecular design of the π-conjugated organic high-spin systems.[1] We have first reported the spin manipulation using the photo-excited molecular field in purely organic π-conjugated spin systems, in which two dangling radical spins align to be parallel through the excited triplet spin coupler, leading to the photo-excited quintet ($S = 2$) high-spin state.[2–4] Thus, the nature of the exchange coupling between two dangling radical spins through the spin coupler changes from antiferromagnetic to ferromagnetic upon the photo-excitation.

Although the several high-spin excited states arising from the spin coupling between the triplet excited state and dangling radicals have been reported,[2–9] all of them except of our systems[2–4] are sigma-bond linked systems[5,8,9] or coordination metal-complexes,[6,7] in which the spin exchange interactions are small in magnitude. π-Conjugated spin systems have the following advantages in the viewpoint of the material science and molecular magnetism: (1) π-Conjugation leads to the strong exchange coupling which is one of the important conditions of the appearance of the balk magnetism at finite temperature. (2) One can well design and synthesize the proper spin systems with the desired spin states using the well-established synthetic chemistry. (3) An enhanced intersystem crossing (ISC) mechanism arising from the attachment of the radical species is available.[2–4] This leads to open a way of the direct ESR detection of the silent photo-excited states.

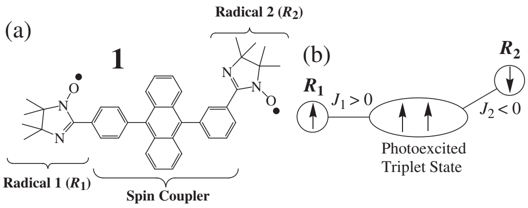
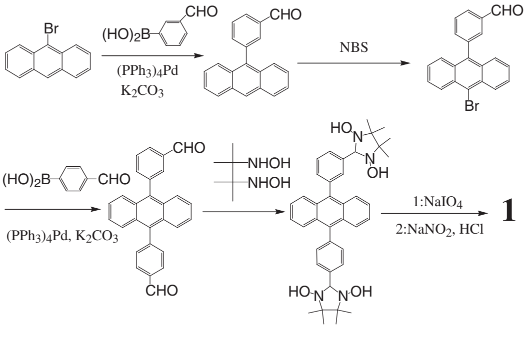


Figure 1. π-Topologically designed molecule and its expected photo-excited spin states. (a) Molecular structure of **1**. (b) Expected spin alignment in the lowest photo-excited states.

In this paper, we have designed and synthesized the molecule **1** and detected a quite interesting photo-excited triplet state constructed from the four unpaired electrons using the above-mentioned advantages. For the spin systems with four unpaired electrons, the spin states with $S = 2$, 1, and 0 exist and normally either the low-spin ($S = 0$) or the high-spin ($S = 2$) state is expected as the lowest photo-excited state. However, one can design a proper molecule with the intermediate spin ($S = 1$) as the lowest photo-excited state by taking π-topology into account. According to our previous works,[2–4] *meta*-joint configuration between the iminonitroxide radical and the triplet excited state of the anthracene moiety leads to the antiferromagnetic coupling and *para*-joint configuration is ferromagnetic coupling between them. Therefore, as illustrated in Figure 1, **1** is expected to have the state with intermediate spin ($S = 1$) as the lowest photo-excited state. The photo-excited triplet state will have an interesting electronic structure in viewpoint of the spin correlation.

1 was synthesized according to Scheme 1.[10] The solution ESR spectrum was well analyzed by a spectral simulation. The hyperfine coupling constants of the four nitrogen atoms in **1** were determined to be $A_N(1) = 0.465$, $A_N(2) = 0.250$, $A_N(3) = 0.414$, and $A_N(4) = 0.210\,\mathrm{mT}$, showing the two iminonitroxide units attached at the asymmetric positions (*meta* and *para* positions). The purity of the sample was higher than 99%, which was confirmed by the magnetic susceptibility measurement. In order to study the photo-excited state, time-resolved ESR (TRESR) experiments were carried out at 30 K using the glass matrix (isopentane:diethylether = 2:3). The details of our TRESR setup were described previously.[3] TRESR spectrum of **1** observed at 0.5 µs after the laser excitation ($\lambda = 355\,\mathrm{nm}$) is shown in Figure 2, together with the simulation. There was no decomposition during the long time accumulation, which was checked by no change of the ESR spectra before and after the TRESR experiments. The TRESR spectrum was very well simulated by the superimposition with equal weight of a triplet and quintet



Scheme 1. Synthetic procedures of molecule **1**.

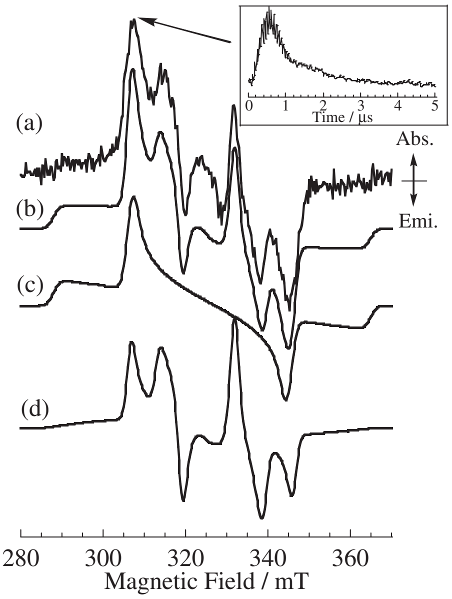


Figure 2. TRESR spectrum of **1**. (a) Observed spectrum. (b) Simulation (superimposition of the triplet (c) and the quintet (d) spectra). (c) Simulation of the triplet state. (d) Simulation of the quintet state.

spectrum. The spin Hamiltonian parameters of the triplet state were determined to be $g = 2.0045$, $D = 0.0360\,\mathrm{cm}^{-1}$, and $E = 0.0\,\mathrm{cm}^{-1}$, and for the quintet state, $g = 2.0050$, $D = 0.0125\,\mathrm{cm}^{-1}$, and $E = 0.0\,\mathrm{cm}^{-1}$. Both states were selectively populated to the lowest energy M_s sublevels in zero field. Interestingly, this initial electron spin polarization (ESP) of the quintet state differs from that of the π-topological isomer with the lowest quintet state[3] and the spectrum at 2.0 μs (after decay of the triplet signal) was simulated by the pure quintet state with ESP close to the previously reported one.[3] The decay profile shows the existence of two components with different lifetimes (the inset of Figure 2), supporting the superimposition of the triplet and quintet signals shown by the simulation. The magnitude of D of the triplet state is ca. 50% of that of anthracene. This small D value is explained well as follows. We treat the whole spin Hamiltonian for the triplet-bis(radical) system given by

$$H_{spin} = H_{ex} + \beta_e H \cdot g^T \cdot S^T + S^T \cdot D(\mathrm{T}) \cdot S^T + \beta_e H \cdot g^{R1} \cdot S^{R1} + \beta_e H \cdot g^{R2} \cdot S^{R2} \quad (1)$$

$$H_{ex} = -2J_1 S^{R1} \cdot S^T - 2J_2 S^T \cdot S^{R2} \quad (2)$$

Here, we omitted other dipolar interactions because their magnitudes are much smaller than the fine-structure tensor of the spin coupler (D(T)). Since in the π-conjugated spin systems, the exchange interaction is normally much larger than other interactions in Eq 1, we first obtained the energies and spin eigenfunctions by diagonalizing H_{ex} and calculated the expectation values of the fine-structure term by using the eigenfunctions. The solutions were obtained analytically and the result was tested by the exact numerical diagonalization of Eq 1. There are two kinds of the triplet states (T_1 and T_2), one quintet state (Qu) and one singlet state (S). The energy vs J_2/J_1 diagram and the reduction factor (f) of the fine-structure tensor ($D = \mathrm{f} \cdot D(\mathrm{T})$) for each spin states are shown in Figures 3a and 3b, respectively. The reduction factor was estimated to be $\mathrm{f} = 0.48$ from the ratio $D(\mathrm{T}_1)/D(\mathrm{Qu})$, determined in this experiment. This f value corresponds to $J_2/J_1 = -0.05$ in Figure 3b. The sign and magnitude of the exchange coupling between the radical moiety and the triplet spin coupler is proportional to the product of the spin densities at linking positions. The sign of the spin densities of the spin coupler linked by two radical moieties is opposite and the spin density for R_2 is expected to be small. Therefore, the small negative value of J_2/J_1 is reasonable. The quintet state is located very closely above the triplet state in this case. The observation of the quintet state in **1** is well understood from this situation.

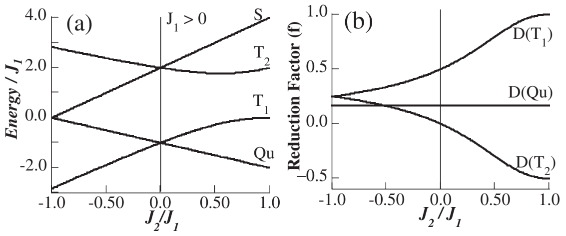


Figure 3. Energy diagram and reduction factor of D tensor.

These results show that **1** has the lowest photo-excited states with an interesting electronic structure in viewpoint of the spin correlation, in which the triplet and quintet states degenerate nearly. This is the first direct detection of the photo-excited triplet state with the reduced D value[11] which comes from the unique electronic structure as the result of the antiferromagnetic spin alignment between the radical spins through the excited triplet spin coupler. This unique photo-excited triplet state will give the ideal target to test the molecular orbital theory for the excited states.

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10 Material **1**: Anal. Calcd for $C_{40}H_{40}N_4O_2$: C, 78.92; H, 6.62; N, 9.20%; Found. C, 78.76; H, 6.71; N, 9.01%.
11 The intermediate triplet state was preliminary reported for a fullerene-bis(nitroxide). (M. Nishimura et al., Abstract of the 79th Annual Meeting of the JCS, 2C3-16 (2001).). However, the D value is close to the triplet state of fullerene derivative. The triplet state with the reduced D value was not observed.

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