Theory of Electronic Control of Spin Alignment in π-Conjugated Molecular Magnets

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Molecular magnetism has attracted considerable interests for decades. Recently a new class of purely organic molecular magnets has received increasing attention as their spin alignment is controllable by external stimuli such as charge doping or photoexcitation, as schematically shown in Fig. 1. Among these pioneering studies, Izuoka and his co-workers have succeeded in controlling intramolecular spin alignment by charge doping in a newly designed organic molecule, thianthrene bis(nitronyl nitroxide) [1]. This molecule, consisting of π-conjugated moiety and two stable radicals, is spin singlet ($S=0$) in its ground state and becomes spin quartet ($S=3/2$) upon one-electron oxidation. The control of spin alignment by photoexcitation has also been demonstrated in a similar type of molecules by Teki [2].
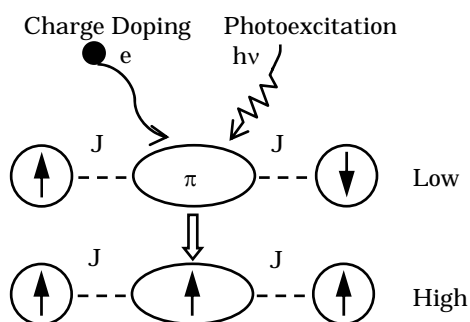

Fig. 1 Schematic picture of spin alignment control by charge doping or photoexcitation.

To design novel functional molecular magnets, it is necessary to theoretically clarify the behavior of spin alignment not only in the ground state, in which the dominant mechanism of spin alignment has been well established as the topological rule, but also in the doped or excited states. However the topological rule cannot be applied to doped or excited molecules, and most discussions on the spin alignment control so far have been given on the basis of individual molecular orbitals.

In order to elucidate the mechanism of spin alignment in both the ground and doped states, from the general point of view, we applied a microscopic model Hamiltonian approach [3]: two localized spins coupled with an N-site Peierls-Hubbard model, which corresponds to π-conjugated moiety shown in Fig. 2. The localized spins correspond to the unpaired electrons of stable radical groups (R) attached to the π-conjugated moiety. In the π–electron system, the electron transfer, Coulomb interaction, and the lattice distortion are taken into account. The two localized spins interact indirectly to each other through the exchange interaction between the spins and π electrons while a direct spin-spin interaction is neglected in this model.

We exactly diagonalized the electronic part of the Hamiltonian by the Lanczos algorithm. Then the lattice is treated classically and optimized by means of the Hellmann-Feynman force

equilibrium condition.

The main target of this study is to determine the change of radical-spin alignment by one electron oxidation in the π–electron system. As an example, we consider two systems: (a) polyene with ten carbons and (b) anthracene with fourteen carbons, as shown in Fig2. For (a) polyene, the neutral ground state ($N_e=N$) is a spin singlet ($S=0$) with antiparallel alignment of radical spins, and bond alternation appears in the lattice. If an electron is removed from the π–conjugated moiety, the doped molecule ($N_e=N-1$) is a spin quartet ($S=3/2$) with parallel alignment of radical spins, leading to controllable spin alignment by doping between the low- and high-spin configurations. The hole-doping also reduces the bond alternation, which is much weaker than that of the neutral case.
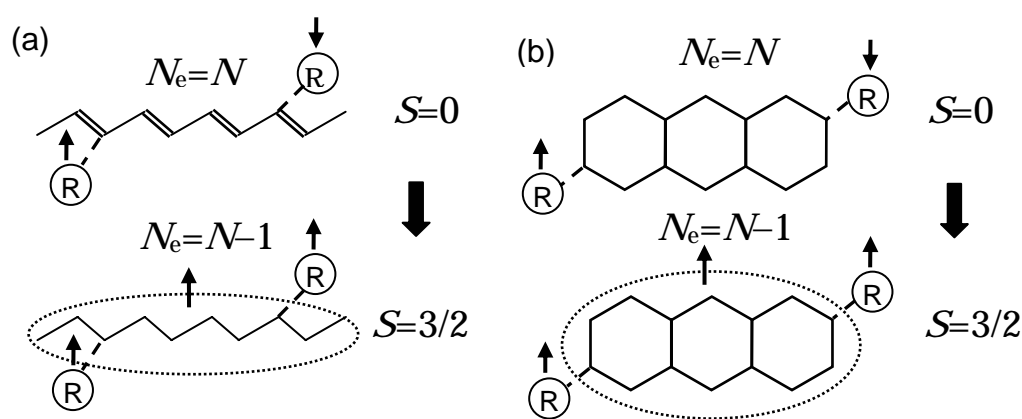

Fig. 2 Schematic picture of spin alignment control by hole-doping in π-conjugated molecules: (a) polyene, (b) anthracene. N_e is the number of π electrons and N is the number of carbons. R denotes the position of an attached radical.

For (b) anthracene, single hole-doping into the π-electron system changes alignment of the radical spins in a similar way as that occurs in polyene, resulting in a transition from a low spin state ($S=0$) to a high spin one ($S=3/2$).

The intramolecular spin alignment depend on the topological structure of molecule, e.g. the doped molecule can be a spin doublet ($S=1/2$) if the radicals are attached to certain sites of π–conjugated part. It is worth emphasizing that the topological effect in the doped molecule is different from that in the neutral state.

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[2] Y. Teki, S. Miyamoto, M. Nakatsuji, and Y. Miura, J. Am. Chem. Soc. **123,** 294(2001).

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