

1A15 Theory of Optical Control of Spin Alignment in π -Conjugated Molecular Magnets

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【 Introduction 】 Clarifying the mechanism of photoinduced high-spin in π -conjugated molecular magnets has become an important theoretical subject, especially after the discovery of controllable spin-alignment by photoexcitation [1, 2]. Teki *et al.* studied molecules composed of two dangling iminonitroxide radicals and a π -conjugated moiety of diphenylanthracene shown in Fig. 1(a). It is demonstrated that these molecules can be excited by photoexcitation from a low-spin state ($S=0$) to a meta-stable high-spin one ($S=2$).

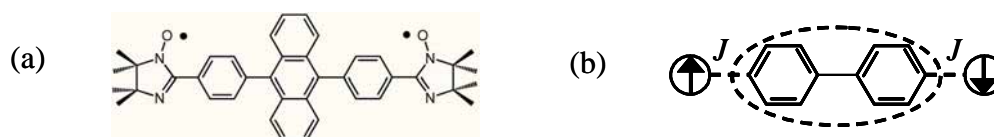


Fig. 1 (a) The molecular structure of diphenylanthracene-bis(iminonitroxide). (b) Schematic picture of biphenyl-based magnetic molecule. The localized spins are coupled to the π -moiety through exchange interactions (J).

【 Theory 】 In order to clarify the mechanism of optically controlled spin-alignment, a general theoretical approach is developed to study magnetic molecules made of π -conjugated moiety and radical groups, based on our previous model for electronic control of spin alignment [3, 4]. The radical spins are replaced by two localized $1/2$ spins, since spin densities tend to be localized in the radical groups. The localized spins interact with π -moiety through exchange interactions, as shown in Fig. 1(b), while a direct spin-spin interaction is neglected. We take long-range Coulomb interactions into account in the π -conjugated moiety, using the Pariser-Parr-Pople model. In this presentation, biphenyl is adopted as the π -moiety. We numerically solved the model Hamiltonian by the exact diagonalization technique, including all the electron-electron and electron-spin correlations.

【 Results 】 We begin our study by exploring spin alignment in molecules with zero dihedral angle between the benzene rings. The calculated energy diagrams are shown in Fig. 2. In the ground state of the topological isomer (a), the localized spins are coupled to each other antiferromagnetically. This spin alignment results in a spin singlet state ($S=0$), as schematically shown in Fig. 2(a). The numerical results reveal that the lowest π -excited state is a spin quintet ($S=2$). The excited triplet of the π -moiety aligns the localized spins in parallel, giving rise to the high-spin state. However, the quintet state cannot be reached directly by photoexcitation since it is optical inactive. To realize such a metastable high-spin state, we should excite π -moiety from the singlet ground state to a highly excited singlet state. After a serial of relaxation processes via intersystem crossing, the π -moiety arrives at the

lowest excited triplet state. Because this state is dipole forbidden, the resultant quintet state has a relatively long lifetime. In the time-resolved ESR observation of diphenylanthracene-bis(iminonitroxide) [1], the high-spin signals are detected 1 μ s after the laser irradiation, and last for almost 10 μ s. Our results offer a theoretical basis to understand the experiment of optically controlled spin-alignment.

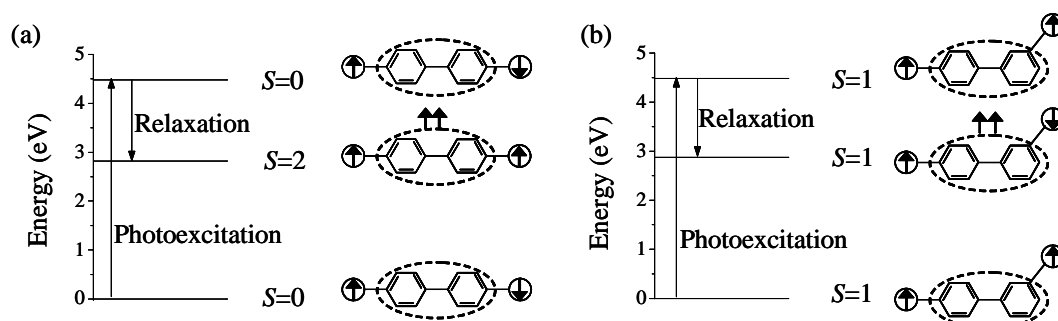


Fig. 2 Energy diagrams of biphenyl-based molecules for topological isomers (a) and (b). The dihedral angle of biphenyl is zero in both molecules.

It is very interesting that spin alignment in the lowest π -excited state exhibits clear dependence on the topology. As shown in Fig. 2(b), one of the localized spins is located at a different position in the topological isomer. The ground state is a triplet corresponding to parallel alignment between the localized spins. The spin alignment can be predicted by the topological rule. However, the lowest π -excited state is triplet ($S = 1$) with antiparallel alignment between the two localized spins. The excited π -moiety plays the role of antiferromagnetic coupler for the localized spins, in contrast to the ferromagnetic one in the case of (a). As a result, meta-stable state in the topological isomer (b) should be such a triplet. Our results are consistent with the experiment on diphenylanthracene-based molecules [2]. It should be noted that the topological effect of excited states is different from that of the ground state. We further study the dihedral-angle dependence of the spin alignment. Our calculated results show that if the angle exceeds a critical value, the lowest π -excited state can also be a spin quintet even in the case of (b).

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

[2] 手木 芳男、中島 悟, 分子構造総合討論会 2003 講演要旨集 2Da01。

[3] P. Huai, Y. Shimoi, and S. Abe, Phys. Rev. Lett. 90, 207203 (2003).

[4] Huai Ping、下位幸弘、阿部修治, 分子構造総合討論会 2003 講演要旨集 2Ap02。