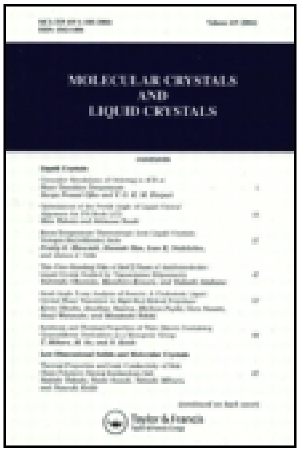

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PREPARATION AND PROPERTY OF IONIC CT COMPLEX OF DIMETHYLAMINO NITRONYL NITROXIDE WITH DDQ

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Abstract An ionic charge transfer complex of dimethylamino nitronyl nitroxide (**DMANN**) was prepared by grinding with **DDQ** in the solid state. An electronic spectrum of the complex showed a broad band at 0.65 eV. The conductivity of the complex was $\sigma \sim 10^{-6}$ S·cm^{-1} at room temperature. The measurement of the magnetic susceptibility revealed that this complex behaves paramagnetically.

INTRODUCTION

Along the rapid progress of molecular magnetism,[1] quite a few organic ferromagnets have been synthesized in these years.[2] The Curie temperatures of purely organic ferromagnets, however, are still extremely low. To realize an organic ferromagnet with high Tc, it is crucial to introduce a stronger intermolecular exchange interaction between organic radicals.

In this respect, it seems promising to utilize a ferromagnetic coupling based on charge transfer interaction proposed by McConnell.[3] In this model, ferromagnetic spin alignment is realized in the charge transfer complex composed of donor (D) and acceptor (A) stacked alternately, because the donor has ferromagnetically coupled spins in the reversed CT state (Figure 1a). Breslow stated a variation of the McConnell's model.[4]

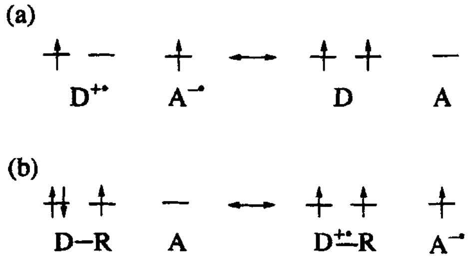
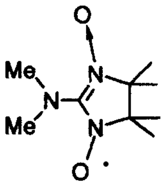


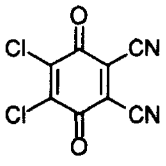
FIGURE 1 Approach to organic ferromagnets based on charge transfer interaction. (a) McConnell's model. (b) Yamaguchi's modification.

The ion radical complex prepared according to his model, however, did not show any ferromagnetic intermolecular interaction, because Jahn-Teller distortion removed the degeneracy of HOMOs of the donor.[5] Wudl documented another modification concerning organic ferromagnetic metal, in which mixed valent columns consist of a ground state triplet donor is to be formed.[6] Yamaguchi proposed a new approach to obtain high spin charge transfer complexes composed of open-shell donors based on a spin polarization mechanism (Figure 1b).[7] Although some charge transfer complexes composed of donors carrying a stable radical substituent have been hitherto reported, ferromagnetic properties have not been detected.[8] The reason for the unsuccessful results may be derived from the lack of exchange interaction of a reasonable magnitude between localized spin on the radical site and the π-spin induced on the donor site through the charge transfer interaction.

Recently we have reported some open-shell donors which afford ground state triplet cation diradicals through one-electron oxidation.[9] Among these open-shell donors so far synthesized, *N,N*-dimethylamino nitronyl nitroxide (**DMANN**), which has the simplest structure, exhibited the lowest oxidation potential. Using this donor we succeeded to prepare an ionic charge transfer complex composed of **DMANN** and 2,3-dichloro-5,6-dicyano-1,4-benzoquionone (**DDQ**). In this paper we report the magnetic property of the ionic charge transfer complex and point out the problem of spin alignment based on the charge transfer interaction.



DMANN



DDQ

PREPARATION AND PROPERTIES OF DMANN · DDQ COMPLEX

Since there are severe requirements for obtaining high spin molecular assembly based on the degeneracy of HOMO of a symmetrical donor in the solid state, we decided to explored novel open-shell donors which afford cation diradicals of the triplet ground state through one-electron oxidation. The high spin state of these cation diradicals originates from a spin polarization between an unpaired electron on the radical site and a π-spin generated on the donor site.

Electronic structure of **DMANN**, which we have developed for the above purpose, can be documented as follows in terms of a perturbational molecular orbital method (Figure 2a). HOMO of the open-shell donor should be located above SOMO. This situation is available, if *homo* of the donor site interacts with *nhomo* of the radical site rather than with *somo*, based on the symmetry of the relevant partial molecular orbitals. This electronic interaction raises the energy level of HOMO, which can be confirmed by the change of oxidation potentials from 1.22 V (*N*,*N*-dimethylamine) to 0.53 V (**DMANN**).[10] Such an exotic electronic structure can be maintained if the on-site Coulombic repulsion of SOMO is larger than the orbital energy (ΔE) between HOMO and SOMO. According to the PM3/UHF calculation of **DMANN**, it turns out that a large spin polarization of HOMO places its β spin higher than the α spin of SOMO (Figure 2b).[11] One electron oxidation ought to remove the β spin of HOMO to afford a ground state triplet species.

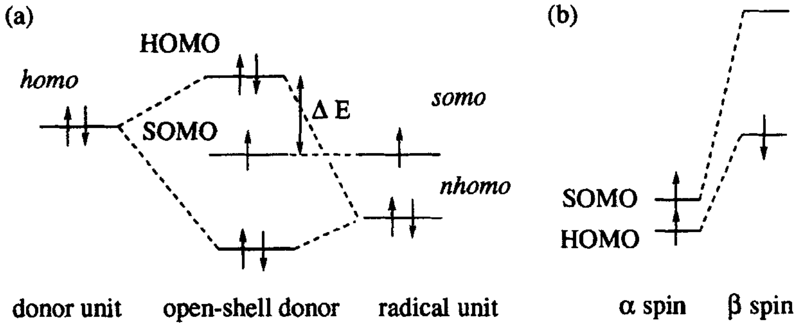


FIGURE 2 Schematic drawings of the electronic structure of open-shell donors. (a) A perturbational MO description. (b) An UHF description.

Grinding **DDQ** with blue crystals of **DMANN**[12] by an agate mortar and pestle in an equal molar amount under a nitrogen atmosphere, we obtained black powders. All attempts to obtain single crystals have been unsuccessful. VIS-NIR spectrum of the **DMANN·DDQ** complex in a KBr pellet showed a broad band in a range of 1750-10000 cm^{-1} with a maximum absorption at 5300 cm^{-1} (0.65 eV), which is assignable to a CT band of very low energy (Figure 3). The IR spectrum of the complex was totally different from those of the neutral compounds (Figure 4). A relatively broad absorption appeared at *ca.* 1500 cm^{-1}. Furthermore, the CN-stretching of **DDQ** in the complex was observed at 2219 cm^{-1}, while those of neutral **DDQ** and $\mathbf{K^+DDQ^-}$ were at 2234 cm^{-1} and 2217 cm^{-1}, respectively.[13] These results indicate that the complex is in an ionic charge transfer state. When the ratio of **DDQ** was increased, only signals of excess **DDQ** appeared in the spectrum of DMANN·DDQ, suggesting that DMANN and DDQ form a stable 1:1 complex.

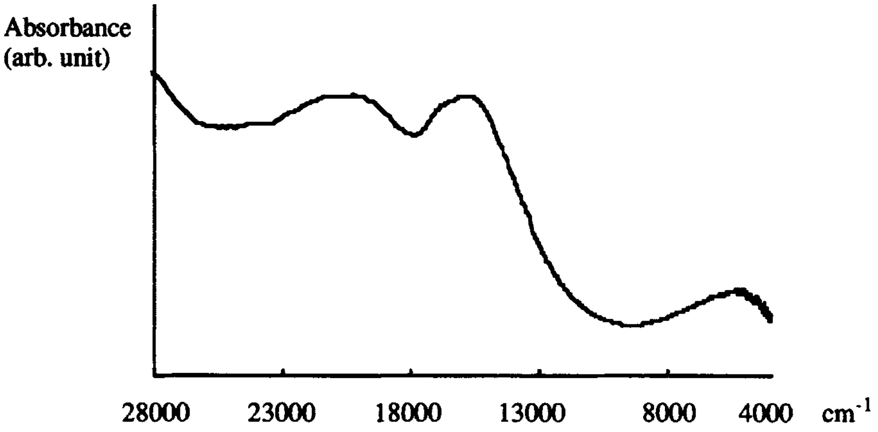


FIGURE 3 VIS-NIR spectrum of DMANN·DDQ.

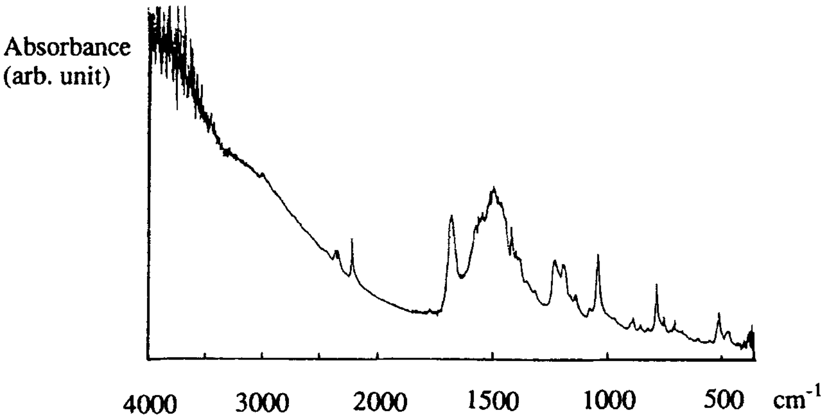


FIGURE 4 IR spectrum of DMANN·DDQ.

Conductivity of the freshly prepared complex in a compressed pellet was measured by means of a two-lead method. The complex showed a poor conductivity ($\sigma = -10^{-6}$ $S \cdot cm^{-1}$) at room temperature. Temperature dependence of magnetic susceptibility of the complex was measured by a Faraday method at temperatures from 3K to 270 K. The magnetic property of the complex revealed to be basically paramagnetic as shown in the $\chi_p T$ *vs*. T plot (Figure 5). The Curie constant was 0.254 at higher temperatures, and this value was about one-third less than that of the S = 1/2 radical. Although the $\chi_p T$ plot could not be reproduced by Curie-Weiss equation in all through the temperature region measured, a weak antiferromagnetic interaction (θ = -1 K) was at least detected from the plot for lower temperatures. The field dependence of magnetization was measured at 3 K. The curve almost fitted the Brillouin function of S =1/2.

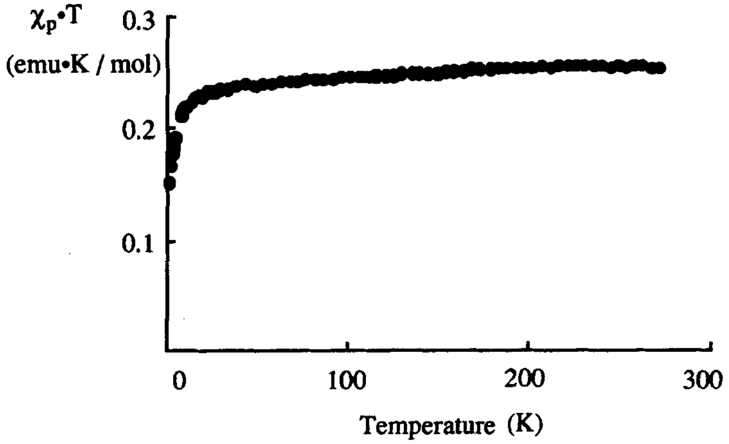


FIGURE 5 Magnetic susceptibility of **DMANN·DDQ**.

DISCUSSION

Cyclic voltammetry revealed that the oxidation and reduction potentials of **DMANN** and **DDQ** are 0.53 V and 0.59 V, respectively.[10] Judging from the difference of -0.06 V between these potentials, **DMANN** and **DDQ** is considered to form a radical ion salt. This estimation does not conflict with the fact that the wave number of the CN-stretching of **DDQ** complex is close to that of the anion radical salt of **DDQ**. In this complex, there are three kinds of spins, $D^{+\cdot}$, a cation radical on the donor site of **DMANN**; $A^{-\cdot}$, an anion radical of **DDQ**; $R^{\cdot}$, a localized spin on the radical site of **DMANN**. The χ_p·T value at higher temperatures, however, was only about two thirds of one paramagnetic spin per complex. The results can be explained as follows. First, electron spins of the cation radical and anion radical are supposed to be coupled strongly in an antiferromagnetic manner, leaving the spin on the radical site as a paramagnetic spin (Figure 6).[8a] This may be derived from a tight overlap between the donor site of **DMANN** and **DDQ**, although we have no structural information at the present stage. Second, the **DMANN·DDQ** complex turned out to be kinetically unstable. In fact, the decomposition of the complex was observed during the magnetic measurement by means of a Faraday balance. The magnetic susceptibility of the complex decreased by *ca.* 15 % in a day at 273 K under a helium atmosphere. Thus the reason for the lack of one third of the predicted value would be caused by the decomposition of the complex.

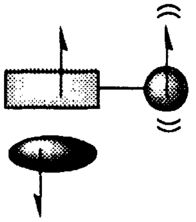


FIGURE 6 A model for an ion-pair.

Yamaguchi has claimed that ferrimagnets may be constructed when triplet cation diradicals and doublet anion radicals are stacked alternately, because of the presence of the antiferromagnetic interaction between them.[14] While the **DMANN·DDQ** complex would satisfy the above requirement, the complex exhibited neither ferro- nor ferrimagnetic intermolecular interactions. This may be partially because of the structure of the complex. Although **DMANN**$^{+\bullet}$ and **DDQ**$^{-}$ are supposed to be tightly overlapped, they would be dimerized in a column if any columnar stacking is formed. Besides the ferromagnetic intramolecular interaction between the π-spin on the donor site of **DMANN** and the localized spin on the radical site may not be significantly large compared with the antiferromagnetic interaction between the cation diradical and the anion radical in order to construct a ferrimagnetic spin system. Consequently, the above two requirements should be examined cautiously in order to construct ferrimagnetic spin systems.

In summary, we prepared an ionic CT complex composed of cation diradical (**DMANN**$^{+\bullet}$) and anion radical (**DDQ**$^{-}$). The temperature dependence of the magnetic susceptibility revealed that the complex behaves paramagnetically. The requirement for constructing organic ferromagnets or ferrimagnets was reexamined based on the experimental result on the present system.

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