

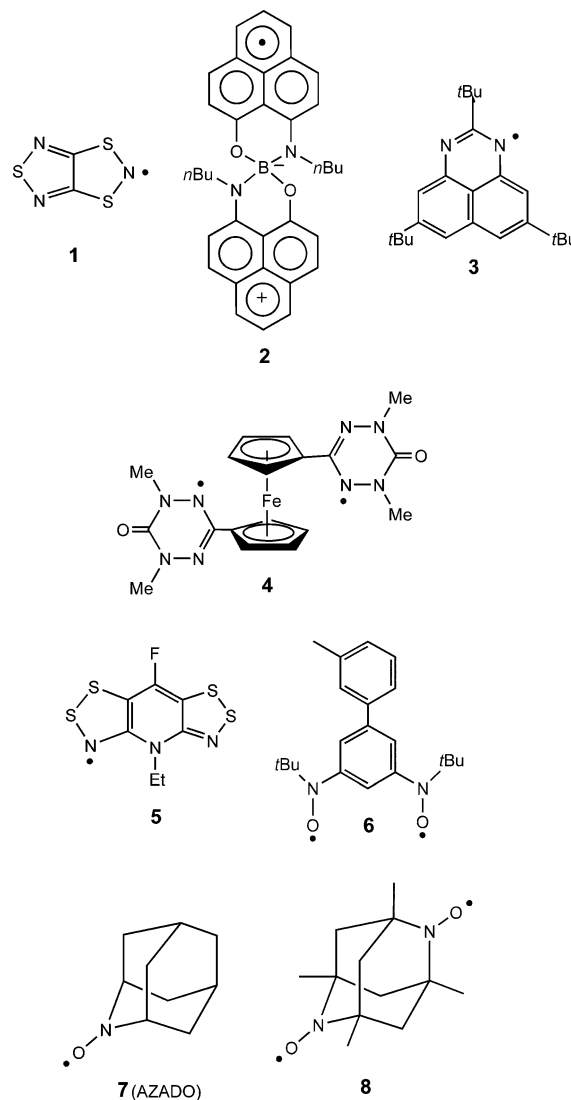
A Functional Nitroxide Radical Displaying Unique Thermochromism and Magnetic Phase Transition**

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The reversible process of color change with temperature known as thermochromism has been observed in a variety of organic compounds, including spiropyrans, salicylidene anilines,^[1] and some transition-metal complexes,^[2] and considerable attention has recently been paid to thermochromic compounds in relation to their potential applications for thermal sensors as well as display, memory, and switching devices.^[3]

In turn, it is only recently that some radical compounds have been found to exhibit thermochromism being coupled with magnetic phase transitions in the solid state.^[4] For example, a large first-order magnetic phase transition was observed in 1,3,5-trithia-2,4,6-triazapentalenyl (TTTA; **1**) with a wide thermal hysteresis loop over the temperature range 230 to 305 K together with the corresponding thermochromism.^[5] An intriguing phenalenyl radical **2** was reported to show magneto-opto-electronic bistability with a hysteresis wind of around 20 K,^[6] and fully reversible continuous thermochromism was found in a diazaphenalenyl **3** being based on the coexistence of its σ - and π -dimers.^[7] An intramolecular π -dimer was clarified in a ferrocene-based verdazyl diradical **4** in the solid state, which dissociated into a colored diradical form in solution.^[8] Hysteretic spin-crossover behavior was disclosed in bisdithiazolyl radical **5** and its unique hypervalent σ -dimer,^[9] and a two-step spin-transition-like behavior was observed in 3'-methylbiphenyl-3,5-diyl bis(*tert*-butyl)nitroxide (**6**).^[10]

2-Azaadamantane *N*-oxyl radical (AZADO; **7**) is an interesting mononitroxide radical among nitroxide families^[11] having adamantane-like caged structure, and it is stable against disproportionative decomposition to the nitrone and the hydroxylamine moieties. The radical compound was primarily prepared by Dupeyre and Rassat^[12] and used



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recently as an effective catalyst for oxidation of alcohols.^[13] It has a similar molecular structure with an eminent ferromagnet 1,3,5,7-tetramethyl-2,6-diazaadamantane *N,N'*-dioxyl (**8**) having a Curie temperature of 1.48 K.^[14] The difference of nitroxide compounds **7** and **8** from the previous radicals **1–6** is that these two radicals have nonplanar and cage structures with unpaired electrons localized at NO moieties, whereas the others have delocalized unpaired electrons over the π -electronic systems. Even if radical **6** has nonplanar and unsymmetrical molecular structure, the unpaired electron is sufficiently delocalized on the π -system.

During our studies dealing with AZADO (**7**), we found by chance that it shows reversible change of color by heating or

cooling around ambient temperature and then investigated the thermochromism together with the magnetic properties. We report herein the structures and the physical properties of AZADO.

As shown in Figure 1, although the color of AZADO is yellow at low temperature (4°C), it gradually changes to reddish brown near room temperature (35°C). The change of reflectivity in AZADO was measured by using a color-difference meter. A sample of AZADO, which had been stored in a refrigerator (4°C), was put on the sample stage of the color-difference meter and the spectrum was continuously measured. The color of the sample gradually changed from yellow to red as the temperature of the sample approached room temperature. At the same, the reflectivity at 600 nm decreased along with the increase of temperature as shown in Figure 2.

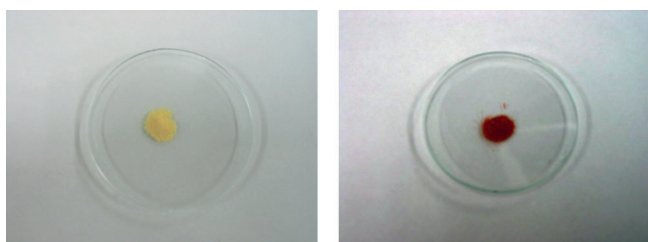


Figure 1. The appearance of **7** at 4°C (left) and 35°C (right).

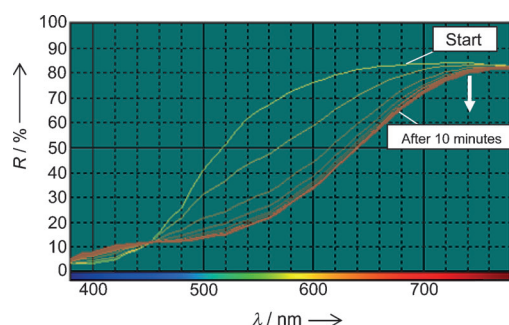


Figure 2. Change of reflectance of **7** obtained by color-difference meter every minute for 10 min.

This phenomenon is observed only for high-purity AZADO and not observed for low-purity (ca. 90%) AZADO. The purity of AZADO was determined by gas chromatography, and the corresponding hydroxylamine derivative (AZADOH) together with the amine derivative (AZAD) were expected to be the main impurities of AZADO. A testing method for its purity analysis has been developed by using an SI-1 column. To confirm the effect on the molecular structure of AZADO by heating, thermal analysis and powder X-ray diffraction studies were conducted.

The thermal analyses of AZADO were performed by means of differential scanning calorimetry (DSC) as well as thermogravimetry/differential thermal analysis (TG/DTA). Because the color of AZADO changes near room temper-

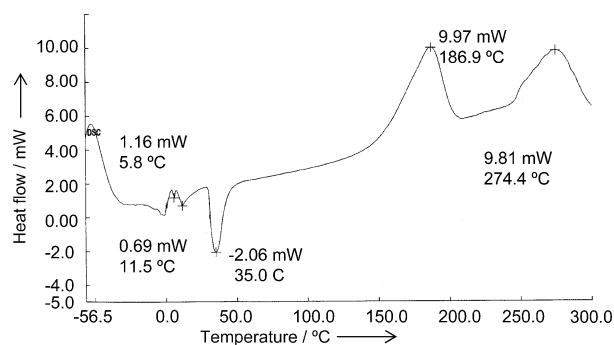


Figure 3. DSC chart of high purity sample of **7** in the temperature range -55°C to 300°C.

ature, the DSC measurement was done from -55°C to 300°C. As shown in Figure 3, a characteristic endothermic peak was observed at about 35°C for a pure sample of AZADO, and the appearance of this endothermic peak was found to be reproducible. That is, after an endothermic peak due to an increasing temperature was detected, the specimen was cooled until the appearance became yellow, then an endothermic peak was detected again with a increasing temperature. In contrast, no endothermic peak was detected when testing the crude AZADO nor was a color change observed in that case (see the Supporting Information).

The powder X-ray diffraction results of a pure sample of **7** at 4°C and room temperature using the high-temperature X-ray diffraction technique are shown in Figure 4. The diffraction pattern changed depending on the temperature and the change was found to be reversible.

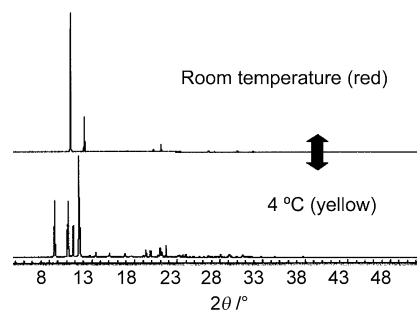


Figure 4. Diffraction patterns of **7** at room temperature and at 4°C.

It was verified from the X-ray analysis at low temperature (LT) that a pure AZADO forms a distinct dimer at low temperature (4°C), having a short bond length between the N and O atoms of about 2.3 Å with a high electron density between the atoms (Figure 5).^[15] However, no exact crystal structure at high temperature (HT, 35°C) could be determined in so far as we have investigated, but such a distinct dimer could not be formed at high temperature, and the color change is considered to be due to the formation of dissociated monomers with possible rotational or vibrational motions, which may be regarded as associated monomers (see the Supporting Information).

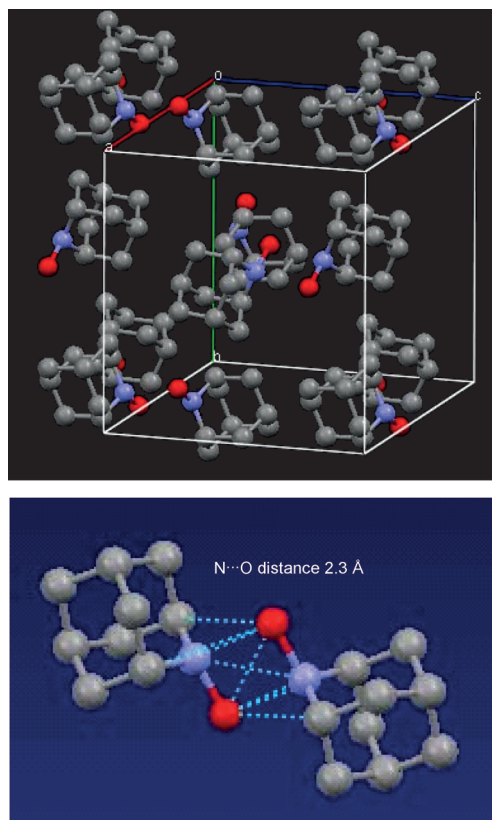
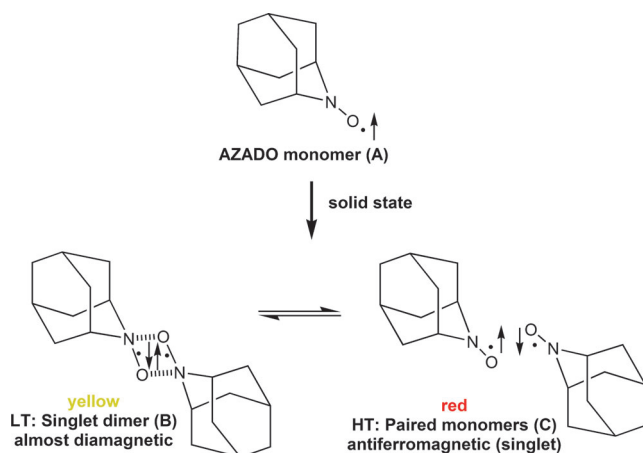


Figure 5. Crystal structure of **7** at 4°C (top) and the structure of a dimer pair at the same temperature (bottom).

Based on the experimental results, we assumed that the thermochromism of AZADO is developed by the change in the molecular complex state due to the change of temperatures. That is, a couple of AZADO molecules form a distinct dimer at low temperature, but it cannot maintain the dimer state at high temperature, and changes the color by the generation of paired monomers with possible rotational or vibrational motions. This situation may be illustrated in Scheme 1, in which the AZADO monomer (A), AZADO



Scheme 1. Possible structures of AZADO monomer (A), dimer (B), and paired monomers with singlet states (C).

singlet dimer with almost a covalent bond (B), and paired monomers (C) are shown as possible species.

We next tried to reconstruct this assumption by means of DFT calculations.^[16] The distance between N and O atoms in the AZADO dimer in the singlet state was calculated to be 2.2 Å (Figure 6), which successfully reproduced the X-ray structural analysis result described above.

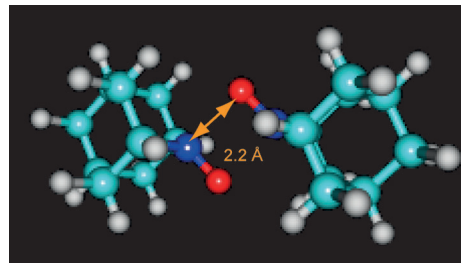


Figure 6. Optimized structure of AZADO dimer.

The UV/Vis absorptions of AZADO monomer (A), a AZADO dimer (B), and paired monomers (C) were then calculated at the TD-B3LYP/6-31 + G(d) level. These calculation results show that AZADO dimer has no absorption in the visible region, while the AZADO monomer has absorptions in the visible light range of around 490 nm (see the Supporting Information). At the same time, bathochromic shifts of the longest wavelength band along with the elongation of intermolecular N–O distance could be verified to imply the coloration of **7** (see the Supporting Information). These results coincide qualitatively with the phenomenon that AZADO dimer changes into paired monomers at high temperature and has an absorption in the visible region, whereas it has no visible absorption at low temperature; that is, no color will be observed.

Thus, the DFT calculation results are qualitatively in satisfactory agreement with the assumption that AZADO forms a dimer (B) at low temperature, but it cannot maintain the distinct dimer state at high temperature and changes color by transition to paired monomers with possible rotational or vibrational motions, which may be regarded as associated monomers (C).^[17]

To see the existence of paramagnetic spin in **7**, its magnetic properties were investigated and at first the EPR spectrum in the solid state was measured at ambient temperature. A singlet peak was observed to confirm the paramagnetic property at an ambient temperature in **7**, whose *g* value and line width (ΔH_{pp}) were estimated to be 2.0065 and 7.8 G, respectively (see the Supporting Information). However, we have so far observed no indication of triplet signals around the half field, and we next investigated its magnetic behavior on a SQUID susceptometer.

The temperature dependence data of magnetic susceptibilities are illustrated in Figure 7. During the heating process (green circles) starting from 2 K, it has a Curie tail (1.7 % spin concentration) at the low-temperature region up to around 50 K with $C = 0.0065 \text{ emu K mol}^{-1}$ and $\theta = 0.17 \text{ K}$ followed by a practically diamagnetic region (LT phase) up to around

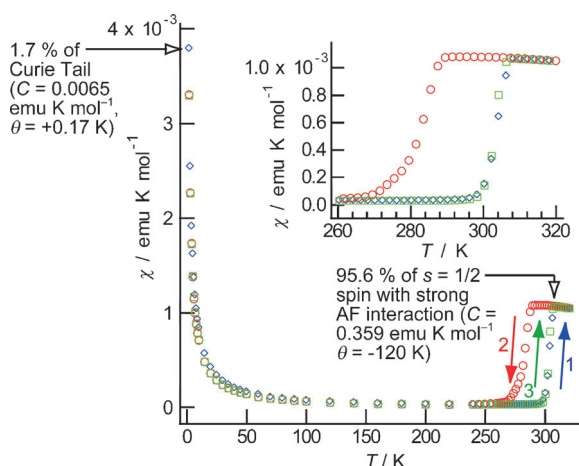


Figure 7. Magnetic susceptibilities of **7** in the temperature range 2 K to 320 K. Blue circles: heating process, red circles: cooling process, green circles: second heating process. Inset: Enlarged range from 260 K to 320 K.

300 K. After that an abrupt increase of magnetic susceptibility is disclosed at around 298 K (25°C, onset temperature) reaching to a maxima of $1.1 \times 10^{-3} \text{ emu K mol}^{-1}$ at 306 K (33°C, HT phase), thus indicating actual generation of paramagnetic spin in the radical **7** and reflecting the color change from yellow to red observed at the temperature. Appreciable AF interactions are estimated for the paramagnetic spins of $S = 1/2$ (95.6% spin concentrations) with $C = 0.359 \text{ emu K mol}^{-1}$ and $\theta = -120 \text{ K}$, respectively. During the cooling process (red circles), in turn, the phase transition initiates at around 286 K (13°C) to revert gradually back to the original diamagnetic state at 260 K (−13°C) with yellow color.

Thus, a thermal hysteresis loop is clearly observed in the magnetic behavior between the temperature range from 260 K to 306 K, revealing it to exhibit a first-order phase transition with a room temperature magnetic bistability. There was little change of the magnetic data for a repeated measurement. The magnetic behavior reminds us of the one observed in TTTA radical **1**,^[5] even if it has a wider loop than the present radical **7**. The difference of the magnetic behavior may be ascribed to that of their molecular and electronic structures, namely, while TTTA is a planar radical and has a delocalized structure of the unpaired electron, AZADO is a nonplanar radical and has a localized structure of the unpaired electron on the NO moiety.

There is another difference between the two radicals, that is, while gradual increase of magnetic susceptibilities was observed in the high-temperature phase for **1**, the values in the high-temperature phase for **7** remain almost constant. Thus, the magnetic behavior of the former radical could be analyzed by 1D antiferromagnetic chain model with $J/k_B = -320 \text{ K}$ and $J'/k_B = -60 \text{ K}$, where J and J' are the intra- and intercolumn exchange coupling constants, respectively, and k_B is the Boltzmann constant. In contrast, the magnetic behavior of the high-temperature phase of **7** could be best fit by the Curie–Weiss model with the Curie constant and Weiss temperature mentioned above. Even if no exact crystal

structure of **7** in the high-temperature phase is available, the difference of their magnetic behaviors should be derived from the difference of their packing features of respective molecules.

Thus, the magnetic data clearly indicate that the almost diamagnetic dimer (B) dissociates to associated and antiferromagnetically coupled monomers (C) with a spin–spin coupling $\theta = -120 \text{ K}$ and exhibiting thermochromism at the same time.

In summary, a nitroxide radical AZADO, was found to be a thermochromic compound, exhibiting reddish brown color near room temperature from the yellow color at low temperature, and a decrease of the reflectivity at 600 nm was observed by measurement with a color-difference meter. A pure sample of AZADO **7** with clear thermochromism displayed an endothermic peak in a DSC measurement and a reversible change of diffraction patterns depending on a change of temperature could be revealed at the same time. It was found from the X-ray analysis of a pure AZADO at low temperature that it forms a dimer (B) at the temperature, whereas no dimer formation could be discriminated at high temperature and then the color change is considered to be due to the formation of paired monomers with possible rotational or vibrational motions, being regarded as associated monomers (C). The experimental results of X-ray analyses at low temperature could be substantiated qualitatively by DFT studies, which also gave a clue of the color change by considering paired and associated AZADO monomers. A hysteresis loop was observed in the magnetic data of **7** in the temperature range 260 K to 306 K, revealing it to exhibit a first-order phase transition with a room-temperature magnetic bistability. During the heating process, a diamagnetic region (LT phase) was observed up to around 300 K followed by an abrupt increase of magnetic susceptibility, reaching a maximum at 306 K, thus indicating actual generation of paramagnetic spin in the high-temperature phase and reflecting the color change from yellow to red observed in the radical compound. At the same time, the negative spin–spin coupling data suggests the formation of paired monomers (C) with antiferromagnetic interaction.

Thus, the present work demonstrates for the first time that nitroxide radicals may also be considered as prototypes for heat-responsive and all-organic magnetic switches.

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