Selective Population from the Excited Multiplet States to the Triplet Ground State in a Phthalocyanine: A New Concept for Controlling Magnetic Properties by Photoexcitation

Kazuyuki Ishii, Yoshiharu Hirose, and Nagao Kobayashi*

Department of Chemistry, Graduate School of Science
Tohoku University, Sendai 980-8578, Japan

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Photocontrol of magnetic properties is an important and intriguing subject, and several methods have been proposed to this end.[1−3] The first is the utilization of light-induced spin crossover in metallocomplexes.[1] In this case, the electronic states of metallocomplexes vary between the low- and high-spin states due to the change in the ligand field strength induced by photoexcitation. The second is the adoption of photochemical reactions, i.e., carbene.[2] In this system, synthesis of the paramagnetic species via the photochemical reaction is employed to control the magnetic properties. The third is an attempt to make use of the photoinduced charge-transfer state.[3] For example, it was reported that the photoexcitation of the charge-transfer band in the Fe−CN−Co complex increases the magnetization.

These phenomena are dependent on a change in the electronic or chemical structures before and after photoexcitation. On the other hand, it is difficult in general to control the magnetic properties by photoexcitation without accompanying the change in the electronic configuration. In this study, a new concept, i.e., photoexcitation control of magnetic interaction between paramagnetic species, is proposed using phthalocyaninatosilicon(IV) (SiPc) covalently linked to two 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) radicals, TEMPO−SiPc−TEMPO (**1** in Scheme 1). The magnetic properties of **1** after photoexcitation were investigated by a time-resolved electron paramagnetic resonance (TREPR) method. We report here the first study on the photoinduced population transfer between the singlet ground (S_0) state and the triplet ground (T_0) state, where the electronic configuration is the same as that in the singlet ground state.

Compound **1** was synthesized as shown in Scheme 1. (Dihydroxy)SiPc (0.063 mmol) and 4-hydroxy-TEMPO (2.5 mmol) were refluxed in toluene (65 mL) in the presence of calcium chloride (2 g) for 2 days. After basic alumina and gel permeation (Bio-Beads SX1, Bio-Rad) chromatography, it was isolated in 15% yield. UV−visible, FAB mass, and elemental analysis were satisfactory.[4] Spectral grade toluene was used for all measurements. Samples were dearated by freeze−pump−thaw cycles. TREPR and steady-state EPR measurements were carried out on a Bruker ESP 300E spectrometer.[5] Samples were excited at 585 nm by a Lumonics HD 500 dye laser pumped with a Lumonics EX 500 excimer laser. The TREPR signals from the EPR unit were integrated using a LeCroy 9450A oscilloscope.

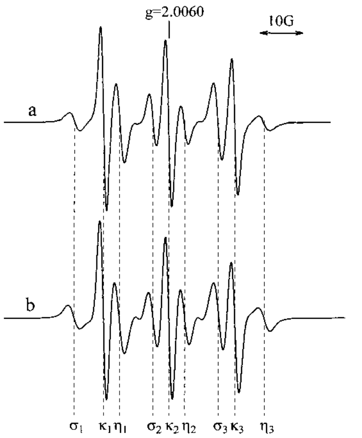
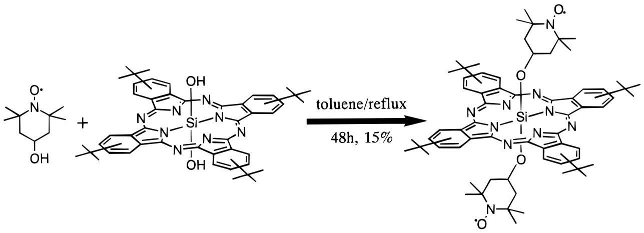


Figure 1. Steady-state EPR spectrum (a) of **1** with its simulation (b).

Scheme 1



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A steady-state EPR spectrum of **1**, observed at 293 K, is shown in Figure 1a. New EPR signals were seen in addition to three signals that are hyperfine coupling (hfc) due to the nitrogen nucleus of TEMPO. These new signals are due to a spin-correlated radical pair constituted by two TEMPO radicals.[6] The Hamiltonian of the spin-correlated radical pair is represented as follows.

$$H_{\mathrm{spin}} = g_1\beta BS_1 + g_2\beta BS_2 + A_{\mathrm{N}}(I_1S_1 + I_2S_2) - J(2S_1S_2 + {}^1/_2) \quad (1)^7$$

A simulation spectrum calculated using eq 1 is shown in Figure 1b.[8] The observed spectrum was simulated well using $J = -5.3$ G.[9] This spectrum is conveniently divided into two groups. One is κ_n ($n = 1-3$), which are the transitions when $m_{\mathrm{N1}} = m_{\mathrm{N2}}$, where the $m_{\mathrm{N}i}$ ($i = 1, 2$) is the magnetic quantum number of the nitrogen nucleus i. The eigenfunctions are represented as $|T_{0+}\rangle$, $|T_{00}\rangle$, $|S_0\rangle$, and $|T_{0-}\rangle$ without the S−T_0 mixing.[10] The other is σ_n and η_n, which are the transitions when $m_{\mathrm{N1}} \neq m_{\mathrm{N2}}$. The eigenfunctions are $|T_{0+}\rangle$, $|T_{0-}\rangle$, $|\Psi_1\rangle$ ($= a|S_0\rangle + b|T_{00}\rangle$), and $|\Psi_2\rangle$ ($= -b|S_0\rangle + a|T_{00}\rangle$) with the S−$T_0$ mixing.[11]

TREPR spectra at 0.6 and 1.8 μs after laser excitation are shown in Figure 2a and 2c, respectively. By comparison with the steady-state EPR spectrum, these signals are assigned to a spin-correlated radical pair in the ground state. The TREPR spectrum at 0.6 μs exhibits an *EEE EEE EEE* polarization pattern. Here, the *E* and *A* denote an emission and an absorption of the microwaves, respectively. On the other hand, the TREPR spectrum at 1.8 μs

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[1] (a) Decurtins, S.; Gütlich, P.; Köhler, C. P.; Spiering, H.; Hauser, A. *Chem. Phys. Lett.* **1984**, *105*, 1. (b) Decurtins, S.; Gütlich, P.; Hasselbach, K. M.; Hauser, A.; Spiering, H. *Inorg. Chem.* **1985**, *24*, 2174. (c) Hauser, A. *Chem. Phys. Lett.* **1986**, *124*, 543. (d) Gütlich, P.; Hauser, A. *Coord. Chem. Rev.* **1990**, *97*, 1.

[2] (a) Itoh, K. *Chem. Phys. Lett.* **1967**, *1*, 235. (b) Wasserman, E.; Murray, R. W.; Yager, W. A.; Trozzolo, A. M.; Smolinsky, G. *J. Am. Chem. Soc.* **1967**, *89*, 5076. (c) Teki, Y.; Takui, T.; Itoh, K.; Imamura, H.; Kobayashi, K. *J. Am. Chem. Soc.* **1986**, *108*, 2147.

[3] Sato O.; Iyoda, T.; Fujishima, A.; Hashimoto, K. *Science* **1996**, *272*, 704.

[4] *m*/*e*: 1107 (M^+). UV−visible (toluene): 681.0 ($\epsilon = 2.7 \times 10^5$), 649.5 ($3.5 \times 10^4$), 611.5 ($4.2 \times 10^4$), 359.0 nm ($8.9 \times 10^4$). Anal. Calcd for $C_{66}H_{82}N_{10}O_4Si$: C, 71.58 H, 7.46 N, 12.65. Found: C, 70.98 H, 7.05 N, 12.51.

[5] Ishii, K.; Fujisawa, J.; Adachi, A.; Yamauchi, S.; Kobayashi, N. *J. Am. Chem. Soc.* **1998**, *120*, 3152.

[6] (a) Glarum, S. H.; Marshall, J. H. *J. Chem. Phys.* **1967**, *47*, 1374. (b) Nakajima, A.; Ohya-Nishiguchi, H.; Deguchi, Y. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 713.

[7] g_1 and g_2 are the *g* factors of electrons 1 and 2, respectively; S_1 and S_2 are the electron spin operators of electrons 1 and 2, respectively; I_1 and I_2 are the nuclear spin operators of nitrogen nuclei 1 and 2, respectively; *B* is the external static magnetic field; β is the Bohr magneton; A_{N} is the hfc constant of nitrogen nucleus; and 2*J* is the singlet−triplet splitting.

[8] The Gaussian line shape function was employed for a single transition. The parameters used are as follows; $g_1 = g_2 = 2.0060$ (± 0.0002); $A_{\mathrm{N}} = 15.4$ G; and $J = -5.3$ G.

[9] Since for most neutral radical pairs *J* is known to be negative, except for several radical ion pairs, the sign of the *J* value was assumed to be negative: Adrian, F. J. *Rev. Chem. Intermed.* **1979**, *3*, 3.

[10] $|T_{0+}\rangle = |\alpha\alpha\rangle$; $|T_{00}\rangle = (|\alpha\beta\rangle + |\beta\alpha\rangle)/\sqrt{2}$; $|S_0\rangle = (|\alpha\beta\rangle - |\beta\alpha\rangle)/\sqrt{2}$; and $|T_{0-}\rangle = |\beta\beta\rangle$.

[11] $a = \cos\theta$; $b = \sin\theta$; and $\tan 2\theta = < S_0|H_{\mathrm{spin}}|T_{00}\rangle/J$.

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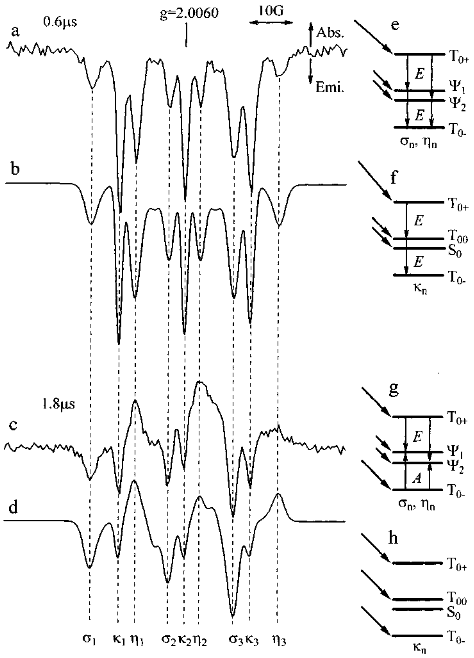

Figure 2. TREPR spectra of **1** at 0.6 (a) and 1.8 μs (c) after laser excitation. Simulation spectrum (b) was calculated using $P(T_{0+}) = 0.5$, $P(T_{00}) = 0.25$, $P(S_0) = 0.25$, and $P(T_{0-}) = 0$ to reproduce the TREPR spectrum observed at 0.6 μs. Simulation spectrum (d) was calculated using $P(T_{0+}) = 0.46$, $P(T_{00}) = 0.24$, $P(S_0) = 0$, and $P(T_{0-}) = 0.3$ to reproduce the TREPR spectrum observed at 1.8 μs. Zeeman energy levels, selective populations from the excited multiplet states, and polarizations were shown for the signals of σ_n and η_n (e and g) and signals of k_n (f and h), respectively.

shows an *EEA EEA EEA* polarization pattern and is obviously different from that at 0.6 μs. The signals of σ_n and η_n at 1.8 μs exhibit three pairs of *E/A* polarizations. From these spectra the populations are analyzed qualitatively as follows. For σ_n and η_n signals, the *E* polarizations at 0.6 μs are interpreted by the relationships, $P(T_{0+}) > P(\Psi_1) \sim P(\Psi_2) > P(T_{0-})$ (Figure 2e), where $P(I)$ denotes the population of the I state.[12] The *E/A* polarizations at 1.8 μs resemble the electron spin polarization of a spin-correlated radical pair generated from the triplet precursor observed for many kinds of photochemical reaction intermediates.[13] This polarization is generated when $P(T_{0+}) \sim P(T_{0-}) > P(\Psi_1) \sim P(\Psi_2)$ (Figure 2g). On the other hand, for κ_n signals, the *E* polarization is produced initially and decays without generating new polarizations. Therefore, the polarizations at 0.6 and 1.8 μs are explained by the relationships, $P(T_{0+}) > P(T_{00}) > P(T_{0-})$ and $P(T_{0+}) \sim P(T_{00}) \sim P(T_{0-})$, respectively (Figure 2f and h). By considering the relationships described above, the TREPR spectra at 0.6 and 1.8 μs should be reproduced using $P(T_{0+}) > P(T_{00}) \sim P(S_0) > P(T_{0-})$ and $P(T_{0+}) \sim P(T_{00}) \sim P(T_{0-}) > P(S_0)$, respectively.

To analyze the TREPR spectra quantitatively, spectral simulations were carried out.[13] The simulation spectrum calculated using $P(T_{0+}) = 0.5$, $P(T_{00}) = 0.25$, $P(S_0) = 0.25$, and $P(T_{0-}) = 0$ is shown in Figure 2b.[14] The TREPR spectrum at 0.6 μs is well reproduced by this simulation spectrum. The spectrum calculated using $P(T_{0+}) = 0.46$, $P(T_{00}) = 0.24$, $P(S_0) = 0$, and $P(T_{0-}) = 0.3$ is shown in Figure 2d. The calculated spectrum reproduces the *EEA EEA EEA* polarization pattern observed at 1.8 μs. Therefore, the initial polarization is due to the excess α spin, and the later polarization is interpreted by selective population to three triplet sublevels in the ground state.

The origins of these polarizations are interpreted as follows. When the excited triplet SiPc is formed, the excited singlet (S_1), triplet (T_1), and quintet (Q_1) states are generated by the interaction among four spins. To investigate the polarization in the excited states, TREPR measurements were carried out at 20K. As a result, an *E* signal in the region of about 3290−3530 G was observed. Since the observed *E* signal is obviously different from that in the ground state, it is assigned evidently to the excited state of **1**. For the spin-allowed internal conversion, the S_1 and T_1 states decay fast to the S_0 and T_0 states, respectively. On the other hand, the lifetime of the Q_1 state is long enough to be observed by TREPR, since the decays from the Q_1 to the T_0 state and from the Q_1 to the S_0 state are spin-forbidden. Therefore, the *E* signal is considered to be due to the Q_1 state.[15] The *E* polarization in the excited state is interpreted by selective intersystem crossing to the Q_1 state in analogy with the excited quartet state.[5,16,17] It has been reported for C_{60}−TEMPO systems that the origin of the polarization in the doublet ground state is the polarization generated in the excited quartet state.[17] Accordingly, the excess α spin at 0.6 μs in the ground state is assigned to the polarization generated in the excited state.

The later polarization was interpreted by selective population to three triplet sublevels in the ground state. The decay from the Q_1 state to the T_0 state should be faster than that to the S_0 state, because the change in the spin quantum number between the Q_1 and T_0 states, $\Delta S = 1$, is smaller than that between the Q_1 and S_0 states, $\Delta S = 2$. Further, since there is the Q_1 state in the Boltzmann distribution after the spin−lattice relaxation, nearly equal population to three triplet sublevels in the ground state can occur. Therefore, the later *E/A* polarization is reasonably interpreted by selective decay from the Q_1 state in the Boltzmann distribution to three triplet sublevels in the ground state.

It was found that the decay from the excited multiplet states to the triplet ground state was selective. In general, it is very difficult to change the difference in the population between the S_0 and T_0 states by varying the temperature, when $|2J| \sim 10^{-3}$ cm^{-1}, as with our biradical. Accordingly, it is interesting that the ground state generated via the excited multiplet states has more triplet character than that without photoexcitation, even at room temperature. Further, it is different in principle from the previous mechanisms, where the magnetic properties are varied by changes in the electronic or chemical structures, to control the magnetic properties using photoinduced population transfer between the S_0 state and the T_0 state, where the electronic configuration is the same as that in the S_0 state. To the best of our knowledge, this kind of mechanism has not been proposed to date. Although the spin polarization decays to the Boltzmann distribution within several microseconds, this mechanism is not only interesting in terms of the physical chemistry but is also useful for controlling the magnetic properties in the ground state by photoexcitation.

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(12) $P(\Psi_1) = a^2P(S_0) + b^2P(T_{00})$; $P(\Psi_2) = b^2P(S_0) + a^2P(T_{00})$.

(13) (a) Sakaguchi, Y.; Hayashi, H.; Murai, H.; I'Haya, Y. J. *Chem. Phys. Lett.* **1984**, *110*, 275. (b) Sakaguchi, Y.; Hayashi, H.; Murai, H.; I'Haya, Y. J.; Mochida, K. *Chem. Phys. Lett.* **1985**, *120*, 401. (c) Buckley, C. D.; Hunter, D. A.; Hore, P. J.; McLauchlan, K. A. *Chem. Phys. Lett.* **1987**, *135*, 307. (d) Tominaga, K.; Yamauchi, S.; Hirota, N. *J. Chem. Phys.* **1990**, *92*, 5175.

(14) Since the difference in the population can be observed by the TREPR method, we assumed that $P(T_{0+}) + P(T_{00}) + P(S_0) + P(T_{0-}) = 1$ and that the minimum $P(I) = 0$.

(15) Further analysis is in progress.

(16) Ishii, K.; Fujisawa, J.; Ohba, Y.; Yamauchi, S. *J. Am. Chem. Soc.* **1996**, *118*, 13079.

(17) (a) Corvaja, C.; Maggini, M.; Prato, M.; Scorrano, G.; Venzin, M. *J. Am. Chem. Soc.* **1995**, *117*, 8857. (b) Corvaja, C.; Maggini, M.; Ruzzi, M.; Scorrano, G.; Toffoletti, A. *Appl. Magn. Reson.* **1997**, *12*, 477.