Electron Spin Polarizations of Phthalocyaninatosilicon Covalently Linked to One TEMPO Radical in the Excited Quartet and Doublet Ground States

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Received: September 3, 1998; In Final Form: January 8, 1999

Phthalocyaninatosilicon(IV) covalently linked to a 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) radical, SiPc-TEMPO, has been studied by time-resolved electron paramagnetic resonance (TREPR). A TREPR spectrum at 20 K is assigned to the doublet ground (D_0) state and the excited quartet (Q_1) state consisting of the excited triplet SiPc and the doublet TEMPO radical. The excited quartet spectrum is simulated using zero field splitting parameters $D = 4.3 \times 10^{-3}$ and $E = 3.3 \times 10^{-4}$ cm^{-1}. The D value observed is almost identical with that calculated under a point charge approximation ($= 4.7 \times 10^{-3}$ cm^{-1}). The electron spin polarization of the Q_1 state is reproduced by selective intersystem crossing (ISC) from the excited doublet states to the $|\pm1/2>$ sublevels in the Q_1 state. This selective ISC is explained by spin−orbit coupling between the P_x and P_y orbitals on oxygen atoms of axial-ligands. In the TREPR spectrum at 293 K, SiPc-TEMPO molecules in the Q_1 and D_0 states exhibit *A* and *E* polarizations, respectively, where the *A* and *E* are absorption and emission of microwaves. The *E* polarization of the D_0 state can be explained by the radical-quartet pair mechanism (RQPM), which originates from an intermolecular interaction between the Q_1 and D_0 SiPc-TEMPO molecules. This RQPM was observed for the first time. The intermolecular interaction between a stable radical and the Q_1 SiPc-TEMPO is clearly demonstrated using a toluene solution containing both SiPc-TEMPO and 2,6-di-*tert*-butyl-α-(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-*p*-tolyloxy (Galvinoxyl). The *A* and *E* polarizations are observed for the fast and slow components of Galvinoxyl, respectively, and can be assigned to the electron spin polarization transfer from the Q_1 SiPc-TEMPO to D_0 Galvinoxyl and the RQPM between the Q_1 SiPc-TEMPO and D_0 Galvinoxyl, respectively.

Introduction

Using a time-resolved electron paramagnetic resonance (TREPR) technique, many kinds of intermediates generated by photoexcitation have been studied in terms of chemically induced dynamic electron spin polarizations (CIDEPs).[1−7] In these studies the electron spin polarizations (ESPs) of the excited triplet states,[1−3] spin-correlated radical pairs,[4,5] the triplet mechanism (TM),[6] and the radical pair mechanism (RPM)[7] have been intensively investigated and have provided important information for many photochemical reactions.

Recently new kinds of CIDEPs, the radical triplet pair mechanism (RTPM)[8−10] and the electron spin polarization transfer (ESPT) mechanism,[11] have been reported, focusing on the interactions between photoexcited triplet species and stable radicals. To obtain novel information, some excited triplet molecules bonded to a stable radical were investigated.[12,13] Corvaja et al. studied C_{60} covalently linked to a TEMPO radical (C_{60}-TEMPO) in toluene solution.[12] In this study, the transition between $|+1/2>$ and $|-1/2>$ in the lowest excited quartet (Q_1) state, which was constituted by the excited triplet C_{60} and doublet TEMPO, was observed for the first time. The CIDEP mechanism was explained by the mixing between the lowest excited doublet (D_1) and Q_1 states originating from the magnetic dipole−dipole interaction. The CIDEP of C_{60}-TEMPO in the doublet ground (D_0) state was also observed, and originated from the ESP generated in the Q_1 state. Namely, the CIDEPs of C_{60}-TEMPO in the Q_1 and D_0 states were produced by the intramolecular interaction. In general, intermolecular interactions are important for CIDEPs in solution, i.e., the RPM, RTPM, and ESPT. Since Q_1 molecules can have both ESPs and zero field splittings (zfs), the ESPT and radical-quartet pair mechanism (RQPM) will be produced by the interaction between the Q_1 molecule and the stable radical in analogy with the radical-triplet system. However, there have been few studies focusing on the intermolecular interaction between the Q_1 molecule and the stable radical. The one and only example is the metalloporphyrin coordinated by pyridyl nitronyl nitroxide radical (MP-nitpy) in toluene solution.[13c] Although the ESPT from the Q_1 MP-nitpy to the nonligating nitpy was discussed in that study, there were several complexities to investigate the intermolecular interaction in solution: (1) Distinguishing between the nonligating nitpy and MP-nitpy was difficult. (2) Dissociation of the axial-ligating nitpy could occur easily in solution.

For these reasons, we have synthesized phthalocyaninatosilicon (SiPc) covalently linked to one 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), SiPc-TEMPO (Figure 1), and studied its CIDEPs at 20 and 293 K by the TREPR method. The summary of important aspects in this research is as follows: (1) A TREPR spectrum of the Q_1 state is observed at 20 K. The magnetic dipole−dipole interaction between the excited triplet SiPc and the doublet TEMPO is examined by comparison with calculation. The ESP mechanism is determined by a spectral simulation. This result is discussed in terms of spin−orbit coupling (SOC) between the Q_1 and higher excited doublet states. (2) For toluene solutions of SiPc-TEMPO and those

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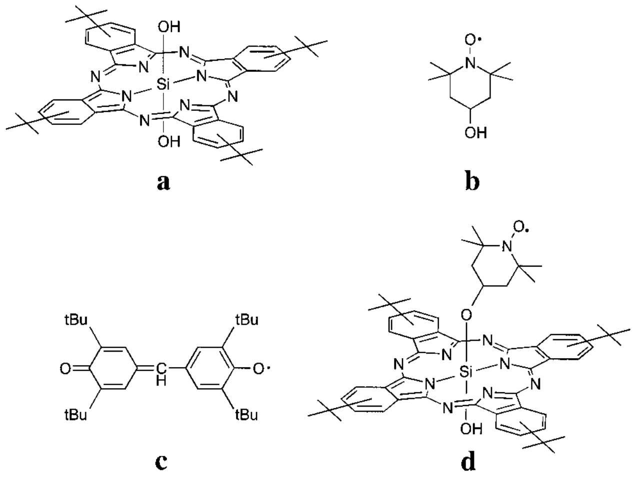

Figure 1. Molecular structures of SiPc$(OH)_2$ (a), TEMPOL (b), Galvinoxyl (c), and SiPc-TEMPO (d).

containing both SiPc-TEMPO and 2,6-di-*tert*-butyl-α-(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-*p*-tolyloxy (Galvinoxyl), TREPR measurements are carried out to investigate the intermolecular interaction. For the SiPc-TEMPO system, the RQPM between the Q_1 and D_0 SiPc-TEMPO is observed for the first time. Further, the ESPT and RQPM between the Q_1 SiPc-TEMPO and D_0 Galvinoxyl are satisfactorily demonstrated for the SiPc-TEMPO−Galvinoxyl system.

Experimental Section

4-Hydroxy-TEMPO (TEMPOL) and Galvinoxyl were purchased from Aldrich Chemical Co. and Tokyo Chemical Industry Co., Ltd, respectively. (Dihydroxy)SiPc (SiPc$(OH)_2$) and SiPc-TEMPO were synthesized following the methods already described.[14] Three signals split by the hyperfine coupling (hfc) of a nitrogen nucleus ($I = 1$) were observed in a steady-state EPR spectrum of SiPc-TEMPO at 293 K, and indicated the presence of a TEMPO radical.[15] Spectral grade toluene (Nacalai Tesque Inc.) was used as solvent, and the concentration of the samples was 1×10^{-3} M. All samples were deaerated by freeze−pump−thaw cycles.

TREPR measurements were carried out at 20 and 293 K on a Bruker ESP 300E spectrometer.[13] An Oxford ESR 900 cold gas flow system was used for the experiments at 20 K. Steady-state EPR measurements were made with the same apparatus. 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 by a LeCroy 9450A oscilloscope.

Results and Interpretations

TREPR Spectra in the Solid State. TREPR spectra of SiPc-$(OH)_2$ and SiPc-TEMPO were observed at 20 K. A TREPR spectrum of SiPc$(OH)_2$ observed at 0.9 μs after laser excitation is shown in Figure 2a (dotted line). From the spectral simulation (solid line), zfs parameters D and E of SiPc$(OH)_2$ in the lowest excited triplet (T_1) state are evaluated as 2.08×10^{-2} and 5.27×10^{-3} cm^{-1}, respectively.[3] The *A*/*E* polarization pattern indicates that intersystem crossing (ISC) from the S_1 state is selective to the T_z sublevel (z: an out-of-plane axis), where the *A* and *E* denote absorption and emission of microwaves, respectively.

A TREPR spectrum of SiPc-TEMPO observed at 0.6 μs after laser excitation is shown in Figure 2b (dotted line). The spectrum exhibits an *AAE* polarization pattern. The splitting between the outer *A* and *E* signals of SiPc-TEMPO is much smaller than that of SiPc$(OH)_2$. The outer *A*/*E* signals of SiPc-TEMPO are similar to those of ZnTPP-nitpy and are assigned to the excited quartet state. For a quantitative discussion, a spectral simulation was carried out. The method of simulation of excited quartet spectra has already been reported.[13b] A simulation spectrum is shown in Figure 2b (solid line) and reproduces the observed *A*/*E* signals. The D and E values of the quartet state are estimated as 4.3×10^{-3} and 3.3×10^{-4} cm^{-1}, respectively. The simulation suggests that the selectivity in the ISC is $P(+3/2):P(+1/2):P(-1/2):P(-3/2) = 0:1:1:0$. To confirm the validity of the zfs parameter, the D value was calculated using the following equation.[13,16]

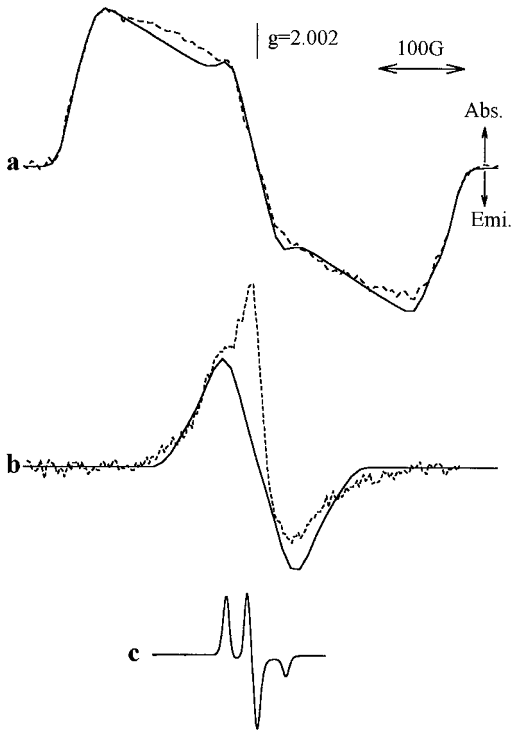

Figure 2. TREPR spectra (dotted lines) of SiPc$(OH)_2$ (a) and SiPc-TEMPO (b) with their simulations (solid lines) and a steady-state EPR spectrum of SiPc-TEMPO (c). TREPR spectra were observed at 0.9 (a) and 0.6 μs (b) after laser excitation. These spectra were observed at 20 K.

$$\boldsymbol{D}(Q_1) = \boldsymbol{D}(T_1)/3 + \boldsymbol{D}(RT_1)/3 \qquad (1)$$

$\boldsymbol{D}(T_1)$ was evaluated from the TREPR spectrum of SiPc$(OH)_2$. $\boldsymbol{D}(RT_1)$ was calculated under a point charge approximation.[17] By diagonalizing $\boldsymbol{D}(Q_1)$, the $\boldsymbol{D}(Q_1)$ value is calculated as 4.7×10^{-3} cm^{-1}. The D value calculated is very close to that observed ($= 4.3 \times 10^{-3}$ cm^{-1}). From this calculation, the outer *A* and *E* signals can be assigned to the Q_1 state consisting of SiPc in the T_1 state (^{3}SiPc*) and TEMPO in the doublet ground (D_0) state (^{2}TEMPO).

In contrast the central *A* signal ($g = 2.007 \pm 0.002$) is assigned to the doublet state, since it cannot be reproduced by the excited quartet state.[13b] To assign the doublet state, the g value of the excited doublet state ($g(D_1)$), which consists of ^{3}SiPc* and ^{2}TEMPO, was calculated as follows.[13,16]

$$g(D_1) = -1/3g(R) + 4/3g(T_1) \qquad (2)$$

$g(T_1)$ was evaluated as 2.000 ± 0.003 from the experiment and $g(R)$ was evaluated as 2.006 from the D_0 TEMPOL. As a result,

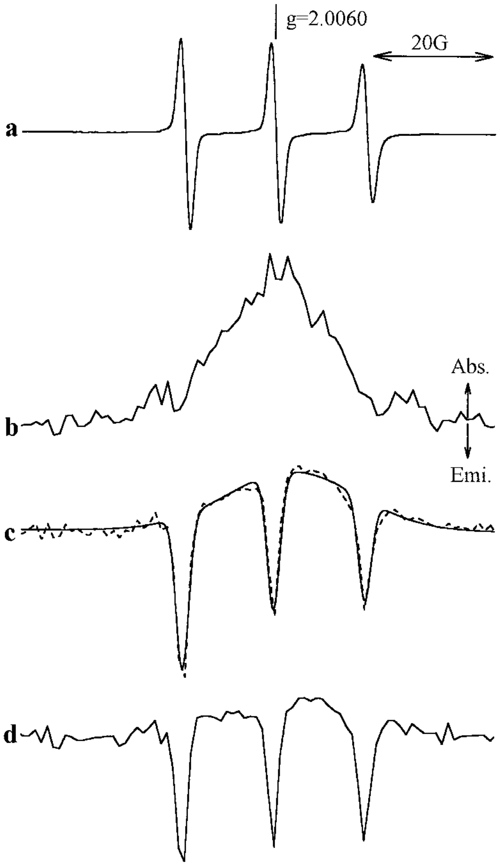

Figure 3. A steady-state EPR (a) and TREPR spectra (b−d) of SiPc-TEMPO. TREPR spectra were observed at 0.1 (b), 1.9 (c), and 3.6 μs (d) after laser excitation. These spectra were observed at 293 K.

$g(D_1)$ is calculated as 1.998 ± 0.003, and is different from the g value observed. A steady-state EPR spectrum of SiPc-TEMPO at 20 K is shown in Figure 2c. It is found that the g value (= 2.007 ± 0.002) of the A signal is almost identical with that (= 2.005 ± 0.001) of the maximal peak position in the steady-state EPR spectrum. Therefore, this A polarization is assigned to the D_0 state.

TREPR Spectra in Solution. TREPR signals of SiPc-TEMPO were observed at 293 K, and TREPR spectra at 0.1, 1.9, and 3.6 μs are shown in Figure 3 with a steady-state EPR spectrum. A spectral simulation was carried out typically for the TREPR spectrum at 1.9 μs. The spectrum is reproduced by using both a broad A signal (g = 2.004 ± 0.002) and three sharp E signals (g = 2.0060 ± 0.0002, hfcc = 15.4 G), as shown in Figure 3c (solid line). The three sharp E signals are assigned to the D_0 state from the g and hfcc values, while the broad A signal is obviously not. The observable excited states in our TREPR experiment (time resolution of 100 ns) are the D_1 and Q_1 states formed by ^{3}SiPc* and ^{2}TEMPO. Since the calculated $g(D_1)$ value (= 1.998) is different from the observed g value, the possibility of the D_1 state can be ruled out. The g value of the Q_1 state ($g(Q_1)$) is expressed as follows.[13,16]

$$g(Q_1) = 1/3g(R) + 2/3g(T_1) \tag{3}$$

Using eq 3, $g(Q_1)$ is calculated to be 2.002 ± 0.003, which is close to the observed g value (= 2.004 ± 0.002). Therefore, this broad A signal can be assigned to the Q_1 state. This assignment is supported by the fact that the Q_1 state in solution is observed for several systems,[12,13c] while the D_1 state has not been observed in solution because of the short lifetime.

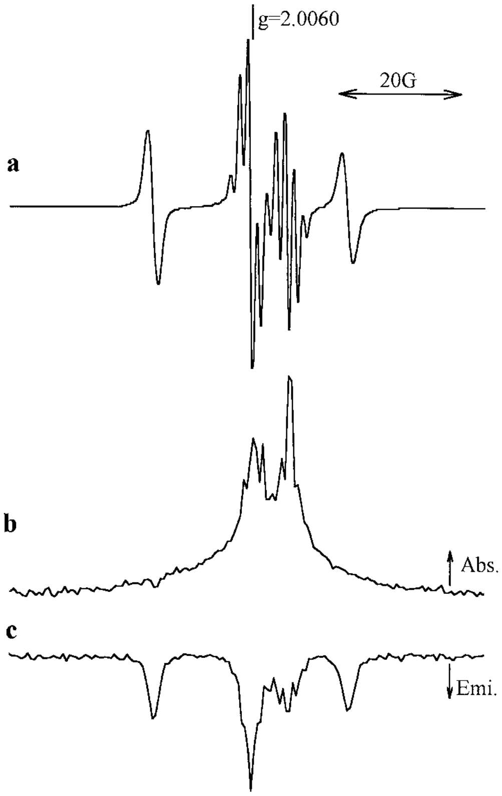

Figure 4. A steady-state EPR spectrum (a) and TREPR spectra (b, c) for the SiPc-TEMPO−Galvinoxyl system. TREPR spectra were observed at 0.6 (b) and 3.4 μs (c) after laser excitation. These spectra were observed at 293 K.

TREPR measurements were carried out for toluene solutions containing both SiPc-TEMPO and Galvinoxyl radical in order to evaluate interactions between the Q_1 SiPc-TEMPO and a stable radical. A steady-state EPR spectrum of the SiPc-TEMPO−Galvinoxyl system is shown in Figure 4a. Since the EPR spectrum of Galvinoxyl is obviously different from that of SiPc-TEMPO, the SiPc-TEMPO−Galvinoxyl system is appropriate for this study. TREPR spectra of the SiPc-TEMPO−Galvinoxyl system at 0.6 and 3.4 μs are shown in Figures 4b and 4c, respectively. Two kinds of signals, a broad A signal and several sharp A signals, are observed in the TREPR spectrum at 0.6 μs.[18] By comparison with the SiPc-TEMPO system, the broad A signal is assigned to the Q_1 SiPc-TEMPO. Since the resonance magnetic fields of the several sharp A signals are consistent with those of the steady-state EPR spectrum of Galvinoxyl, the sharp TREPR signals are assigned to the D_0 Galvinoxyl with ESPs. On the other hand, several E signals are observed in the TREPR spectrum at 3.4 μs. By comparison with the steady-state EPR spectrum, these sharp signals are assigned to the D_0 SiPc-TEMPO and D_0 Galvinoxyl.

Discussion

CIDEP in the Solid State. The spectral simulation of SiPc-TEMPO has revealed that the ISC rates from the higher excited doublet states to the $|\pm 1/2>$ sublevels in the Q_1 state are faster than those to the $|\pm 3/2>$ sublevels. This selectivity originates from coupling between the spin and orbital angular momentum along the out-of-plane axis.[13] To confirm this origin, the SOC between the excited doublet states and the Q_1 state is examined. Since the excitation energy of TEMPO (~20000 cm^{-1}) is much higher than those of the S_1 (~14500 cm^{-1}) and T_1 (~9000 cm^{-1}) SiPc, the excited states constituted by the S_1 or T_1 SiPc have to be considered. In the ZnTPP-nitpy system, the ISC rates to the |±1/2> in the Q_1 state are faster than those to the |±3/2>. This is explained by the SOC due to the d_π orbitals on the zinc ion.[13] However, the d_π orbitals cannot influence the properties of the S_1 and T_1 SiPc, since the energies of d_π orbitals on the Si ion are much higher than that of the LUMO of phthalocyanines. Alternatively, SOC on the oxygen atoms of the axial-ligands is possible. Gouterman et al. studied the excited triplet states of porphyrins and noted the importance of the SOC between the P_x and P_y orbitals of the axial-ligands.[19] The fact that the SOC between the P_x and P_y orbitals on the oxygen atoms is more efficient than that along the in-plane axes is also manifested in the selective ISC of $SiPc(OH)_2$ in this study. Hence, the ESP of the Q_1 SiPc-TEMPO can be reasonably interpreted by the SOC between the P_x and P_y orbitals on the oxygen atoms of the axial-ligands.

The *A* polarization of the D_0 state was observed in the solid state and revealed that the β spin was generated selectively in the Q_1 state. It has been reported that for the C_{60}-TEMPO system the ESP in the Q_1 state is transferred to the D_0 state via an intramolecular process.[12] Therefore, the *A* polarization of the D_0 state is considered to be due to the excess β spin generated in the Q_1 state.

CIDEP in Solution. For the SiPc-TEMPO system at 293 K, the *A* and *E* polarizations were observed for the Q_1 and D_0 SiPc-TEMPO, respectively. The *A* polarization of the Q_1 state in solution is consistent with the ESP in the solid state, where the β spin is generated selectively. This *A* polarization is explained by selective ISC. On the other hand, the *E* polarization of the D_0 state observed in solution is contrary to the *A* polarization of the D_0 state observed in the solid state. The origins of this *E* polarization must be explained.

When SiPc-TEMPO molecules are partially excited, three electronic states, the D_0, D_1, and Q_1 states, are formed in solution. For this phenomenon, two kinds of CIDEP mechanisms due to intramolecular interactions are conceivable. One is the CIDEP of the Q_1 state produced by SOC. Although excess β spin is generated in the Q_1 state as seen in the experiments at 20 and 293 K, this β spin does not provide the *E* polarization of the D_0 state at 293 K. The second is the mixing between the Q_1 and D_1 states by magnetic dipole−dipole interaction. This polarization mechanism was observed for some C_{60}-TEMPO systems,[12] where the ESP of the Q_1 state was transferred to the D_0 state and was the same as that of the D_0 state. However, in our system, the *E* polarization of the D_0 state is the opposite polarization of the Q_1 state. Therefore, it cannot be interpreted by the intramolecular interaction.

Next intermolecular interactions need to be considered. For the interaction between the D_1 and D_0 states, the RPM is possible. However, since the hyperfine dependence is insignificant, the RPM can be neglected.[7] This is supported by the fact that the rate of polarization of the D_0 state is slower than that of the Q_1 state, despite the shorter lifetime of the D_1 state. For the interaction between the Q_1 and D_0 states, two kinds of CIDEPs are probable. One of which is the ESPT from a Q_1 molecule to a D_0 molecule.[11,13c] The ESP of the Q_1 state is the *A* polarization, while that of the D_0 state is the *E* polarization. The *E* polarization of the D_0 SiPc-TEMPO, therefore, cannot be interpreted by the ESPT. The other is the RQPM, which is similar to the RTPM.[8] When a D_0 molecule interacts with a Q_1 molecule, the triplet (T) and quintet (F) states are generated as shown in Figure 5. When $J < 0$ (*J*: an electron exchange interaction), an *E* polarization is expected by zfs interactions in analogy with the RTPM. The insignificant hyperfine dependence observed is similar to that in the RTPM. Consequently, the *E* polarization of the D_0 state in solution can be assigned to the RQPM.

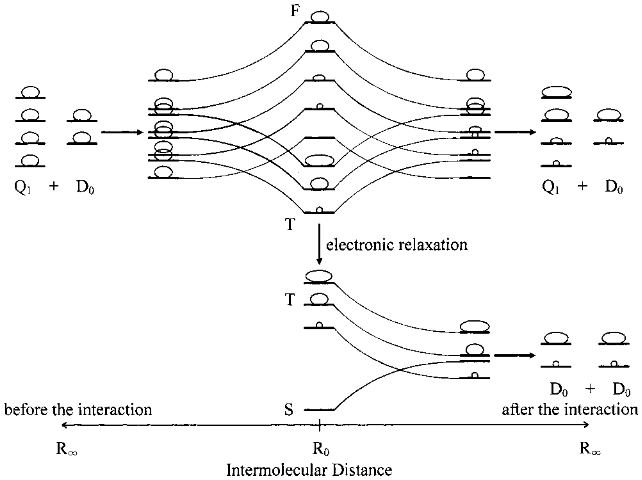

Figure 5. The radical quartet pair mechanism.

For the SiPc-TEMPO−Galvinoxyl system, the intermolecular interaction between Q_1 and D_0 molecules is nicely substantiated. The fast and slow components of the CIDEPs of Galvinoxyl were the *A* and *E* polarizations, respectively. These ESPs are generated by the interaction between the Q_1 SiPc-TEMPO and the D_0 Galvinoxyl and are interpreted with reference to the case of the radical-triplet system. When a stable radical interacts with an excited triplet molecule, two kinds of CIDEPs, i.e., the ESPT and RTPM, are generated. The ESPT occurs initially, and the ESP due to the RTPM is generated after spin lattice relaxation.[11] For the radical-quartet system the ESPT and RQPM are considered. Since the ESP of the Q_1 SiPc-TEMPO is the *A* polarization, an *A* polarization of radicals will be generated by the ESPT mechanism. In contrast, when $J < 0$, the RQPM will provide an *E* polarization. Accordingly, the *A* and *E* polarizations will be produced in that order. Indeed, the fast *A* and slow *E* polarizations of the D_0 Galvinoxyl were observed in the SiPc-TEMPO−Galvinoxyl system. As a result, these *A* and *E* polarizations are assigned to the ESPT and RQPM generated by the intermolecular interaction between the Q_1 SiPc-TEMPO and D_0 Galvinoxyl. The CIDEP mechanism of the SiPc-TEMPO−Galvinoxyl system is summarized in Figure 6.[20] The *A* polarization of the Q_1 SiPc-TEMPO is generated by selective ISC from the higher excited doublet states (D_n). The ESPT occurs from the Q_1 SiPc-TEMPO with the *A* polarization to the D_0 Galvinoxyl. After spin lattice relaxation, the *E* polarizations of the D_0 SiPc-TEMPO and Galvinoxyl are produced by the RQPM.

Conclusions

The CIDEPs of SiPc-TEMPO in solution and in the solid state were studied by TREPR. The TREPR spectrum of SiPc-TEMPO in the solid state was assigned to the D_0 state and the Q_1 state, which consists of ^{3}SiPc* and ^{2}TEMPO. The *D* value of the Q_1 state evaluated by the spectral simulation was almost the same as that calculated under the point charge approximation. The ESP in the Q_1 state was reproduced by selective ISC from the excited doublet states to the |±1/2> sublevels in the Q_1 state. This ISC was explained by the SOC between the P_x and P_y orbitals on the oxygen atoms of the axial-ligands.

For the SiPc-TEMPO system, two components, a broad *A* signal and three sharp *E* signals, were observed at 293 K and were assigned to the Q_1 and D_0 states, respectively. The *E*

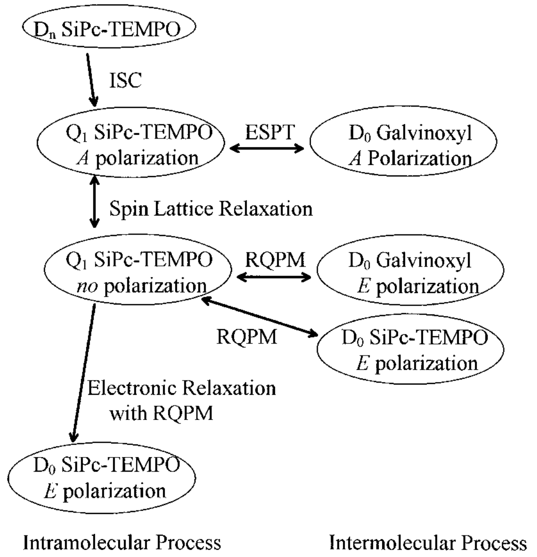

Figure 6. Summary of the CIDEP mechanism for the SiPc-TEMPO−Galvinoxyl system.

polarization of the D_0 state could be interpreted in terms of the radical-quartet pair mechanism. Further, the ESPT and RQPM generated by the intermolecular interaction between the Q_1 SiPc-TEMPO and D_0 Galvinoxyl were nicely substantiated for the SiPc-TEMPO−Galvinoxyl system.

Acknowledgment. This work was partially carried out in Advanced Instrumental Laboratory for Graduate Research of Department of Chemistry, Graduate School of Science, Tohoku University. This work was supported by Grant-in-Aid for Scientific Research on Priority Area “Nanoscale Magnetism and Transport” No. 10130202 and for Scientific Research No. 10740300 from the Ministry of Education, Science, Sports, and Culture, Japan and the Mitsubishi Foundation.

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