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Conditions for forming excited multiplet states: magnetic interactions between excited triplet (phthalocyaninato)zinc and doublet nitroxide radical

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Excited state phthalocyanine complexes comprising (tetra-*tert*-butylphthalocyaninato)zinc (ZnPc) coordinated by nitroxide radicals have been studied by time-resolved electron paramagnetic resonance (TREPR). Five ZnPc complexes coordinated by an axial ligand containing a nitroxide radical NRX (where X (= 4, 5, 6, 8 or 10) denotes the number of bonds from the zinc to the nitroxide nitrogen) were selected, and the magnetic interactions between the excited triplet ZnPc and respective NRX have been investigated in terms of the conditions for forming the excited quartet (Q_1) state. Optimum structures calculated using a PM3 Hamiltonian show that the bond number X is well correlated with the distance between zinc and nitroxide nitrogen atoms (Δr). TREPR spectra of ZnPc complexes, which are coordinated by NR8 or NR10, are almost the same as that of ZnPc coordinated by pyridine (ZnPc–py), indicating that the electron exchange interaction, J, between the excited triplet ZnPc and doublet nitroxide is much smaller than the zero field splitting parameter D value ($D(T_1) = 0.720$ GHz) of the excited triplet ZnPc–py. On the other hand, TREPR spectra of the NR4, NR5 and NR6 complexes are assigned to the Q_1 state constituted by the excited triplet ZnPc and doublet nitroxide radical. The D value of the Q_1 state ($D(Q_1)$) decreases in the order ZnPc–NR6 (0.205 GHz) > ZnPc–NR5 (0.190 GHz) > ZnPc–NR4 (0.165 GHz). This decrease is interpreted in terms of a magnetic dipole–dipole interaction between the triplet ZnPc and doublet nitroxide, which is opposite in sign to $D(Q_1)$, and increases in the order ZnPc–NR6 < ZnPc–NR5 < ZnPc–NR4. Calculations of resonance magnetic fields indicate that the $|J|$ values of the NR4, NR5 and NR6 complexes are larger at least than the $D(T_1)$ value. It is found that the D and $|J|$ values are well correlated with the bond number X and distance Δr. This EPR study is useful for understanding the photophysical and photochemical properties of chromophores.

Introduction

Interactions between phthalocyanines (Pcs) in the lowest excited triplet (T_1) state and other paramagnetic molecules result in some important phenomena in photophysical and photochemical processes. One example is a quenching of Pcs in the lowest excited singlet (S_1) and T_1 states.[1,2] This quenching occurs when the concentration of the T_1 Pc is high or when paramagnetic metals or radicals are present. A second phenomenon is a formation of excited singlet oxygen. Here, a triplet–triplet annihilation between the T_1 Pc and triplet oxygen results in an energy transfer to yield the excited singlet oxygen and this mechanism has been applied to photodynamic cancer therapy.[3] A third phenomenon is photo-induced population transfer (PIPT) between the singlet and triplet ground states, observed for (phthalocyaninato)silicon covalently linked to two doublet nitroxide radicals.[4] This PIPT results from selective decay from the excited states to the triplet ground state, and is, therefore, attractive as a new concept for controlling magnetic properties by photoexcitation. Since a key feature of these phenomena is the formation of excited multiplet states constituted by the T_1 Pc and other paramagnetic molecules, it is necessary to know the conditions under which the excited multiplet states are formed.

Electron paramagnetic resonance (EPR) is a powerful technique for investigating magnetic interactions between paramagnetic species, and accordingly has been applied to many types of paramagnetic molecules in the ground state.[5–9] However, few direct EPR observations of excited multiplet states consisting of the T_1 molecule and other paramagnetic species have been reported because of the short lifetime and weak luminescence. Time-resolved EPR (TREPR) is a useful method for investigating this type of short-lived paramagnetic species, and several TREPR studies have recently been reported in relation to the excited multiplet states, such as the lowest excited doublet (D_1) and quartet (Q_1) states constituted by the T_1 chromophore and doublet nitroxide radical.[10–15] However, conditions for forming such excited multiplet states have not been investigated by changing interactions gradually even for the most intensively studied chromophore–nitroxide systems.[16]

Recently, we studied (tetra-*tert*-butylphthalocyaninato)zinc (ZnPc) coordinated to 4-amino-2,2,6,6-tetramethyl-1-piperidinyloxy radical (NR5), and suggested that this complex was suitable for investigating the Q_1 state.[14b] In this study, we, therefore, have selected four other ZnPc complexes coordinated by an axial ligand containing a nitroxide radical NRX (where X (= 4, 6, 8 and 10) denotes the number of bonds from the zinc to the nitroxide nitrogen) in order to change the interactions between the T_1 ZnPc and doublet nitroxide systematically. The electron exchange and magnetic dipole–dipole interactions between the T_1 ZnPc and respective NRX have been analyzed, focusing on the conditions for forming the excited multiplet states.

Experimental

Materials

4-[((2,2,6,6-Tetramethyl-1-oxypiperidin-4-yl)oxy)carbonyl]-pyridine (NR10) and ZnPc were synthesized by following the methods already reported.[6a,17] Pyridine, *n*-butylamine, and 3-amino-2,2,5,5-tetramethyl-1-pyrrolidinyloxy (NR4) were

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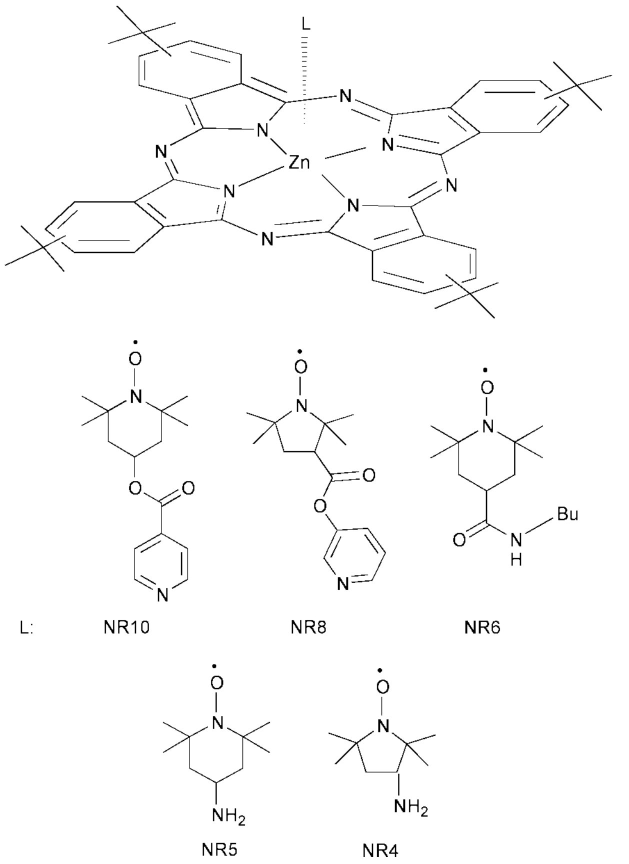

purchased from Wako Pure Chemical Industries Ltd., Nacalai Tesque Inc., and Acros Organics, respectively.

4-[((*n*-Butyl)amino)carbonyl]-2,2,6,6-tetramethyl-1-piperidinyloxy (NR6)

50 μl of isobutyl chloroformate (3.75×10^{-4} mol) were added to 5 ml of a dichloromethane solution containing 25 μl of pyridine and 50 mg of 4-carboxy-2,2,6,6-tetramethyl-1-piperidinyloxy (2.5×10^{-4} mol), stirred at −7 °C under a nitrogen atmosphere. After 30 min, 38 μl of *n*-butylamine (3.75×10^{-4} mol) were added to the solution, and then the solution was stirred at room temperature for 70 h. The reaction mixture was washed with water, and the organic phase was collected and evaporated. After purification by TLC (alumina, dichloromethane), the product was obtained by recrystallization from dichloromethane. Yield 16 mg, 25%; FAB mass spectrum: *m*/*z* 255 (M^+). Anal. Calc. for $C_{14}H_{27}N_2O_2$: C, 65.84; H, 10.66; N, 10.97. Found: C, 65.98; H, 10.45; N, 10.91%.

3-[((2,2,5,5-Tetramethyl-1-oxypyrrolidin-3-yl)carbonyl)oxy]-pyridine (NR8)

70 mg of 1,3-dicyclohexylcarbodiimido (3.2×10^{-4} mol) were added to 5 ml of a dry tetrahydrofuran solution containing 10 mg of 4-(dimethylamino)pyridine, 25.5 mg of 3-hydroxypyridine (2.7×10^{-4} mol) and 50 mg of 3-carboxy-2,2,5,5-tetramethyl-1-pyrrolidinyloxy (2.7×10^{-4} mol), stirred at 0 °C under a nitrogen atmosphere. After 10 min, the temperature was raised to room temperature, and then the solution was stirred for 3 h. The reaction mixture was filtered, and the filtrate was collected and evaporated. After column chromatography (silica, chloroform), the product was obtained by recrystallization from dichloromethane. Yield 36 mg, 51%; FAB mass spectrum: *m*/*z* 263 (M^+); Anal. Calc. for $C_{14}H_{19}N_2O_3$: C, 63.86, H, 7.27, N, 10.64. Found: C, 64.25, H, 7.32, N, 10.74%.

EPR measurements

Spectral grade toluene (Nacalai Tesque Inc.) was used as a solvent for all measurements. Coordination of pyridine or *n*-butylamine to ZnPc was checked by electronic absorption spectra. While the spectral changes were not so large, equilibrium constants were roughly estimated to be larger at least than 10^4 M^{-1}. For EPR measurements, the concentration of ZnPc was 1×10^{-4} M, while those of nitroxide radicals were 10–100 times higher than that of ZnPc. Under these conditions, coordination of axial ligands was almost complete even at room temperature (>90%), and TREPR signals of ZnPc uncoordinated to an axial ligand were absent. All samples were deaerated by freeze–pump–thaw cycles.

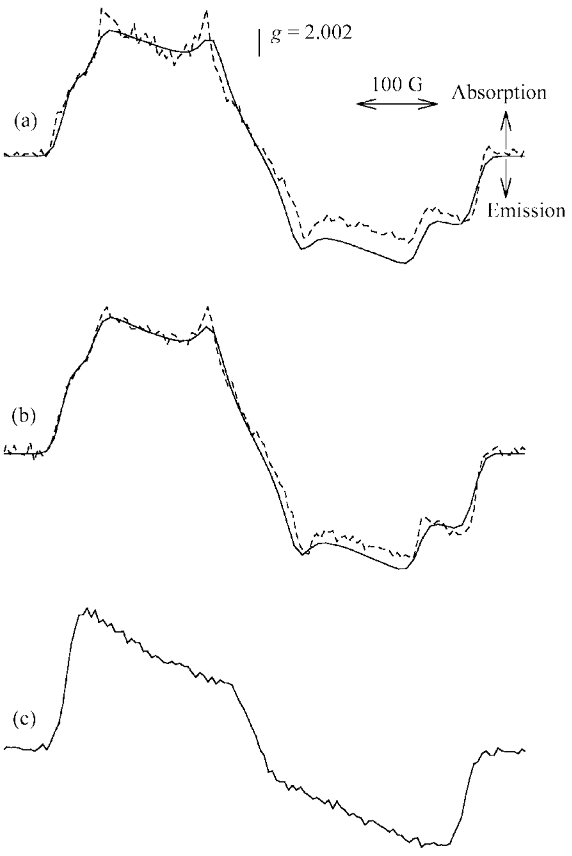

Fig. 1 TREPR spectra of ZnPc–bua (--- a), ZnPc–py (--- b) and ZnPc (c) together with simulations (—— a, b). All spectra were observed at 20 K and 0.5–0.9 μs after laser excitation.

TREPR and steady-state EPR measurements were carried out at 20 K on a Bruker ESP 300E spectrometer.[13,14] An Oxford ESR 900 cold gas flow system was used for controlling the temperature. Samples were excited at 585 nm by a Lumonics HD 500 dye laser pumped with a Lumonics EX 500 excimer laser. TREPR signals from the EPR unit were integrated using a LeCroy 9450A oscilloscope.

Results and discussion

TREPR measurements were carried out for ZnPc coordinated by pyridine (ZnPc–py), and ZnPc coordinated by *n*-butylamine (ZnPc–bua). TREPR spectra of these complexes are shown in Fig. 1(a) and (b), and parameters used for the simulations are summarized in Table 1. Fig. 1(c) shows a TREPR spectrum of ZnPc, which is obviously different from those of ZnPc–py and ZnPc–bua,[18] indicating that coordination of axial-ligands can be verified easily. These spectra exhibit an *A*/*E* polarization pattern (*A*/*E* denotes absorption (*A*) and emission (*E*) of microwaves at the lower and higher magnetic field sides, respectively), and are reproduced by selective intersystem crossing (ISC) to the T_{1z} sublevel (*z*; an out of plane axis). This selectivity is explained by spin–orbit coupling (SOC) of d_π orbitals on the zinc ion between the S_1 state and T_{1z} sublevel.[19]

Table 1 Zfs parameters and sublevel population ratios

Compound	Assignment	D/GHz	E/GHz	$D(Q_1)_{calc}$/GHz	Sublevel population ratio[a]	Δr/Å
ZnPc–py	Triplet	0.720	0.140	—	0 : 0 : 1	—
ZnPc–bua	Triplet	0.720	0.140	—	0 : 0 : 1	—
ZnPc–NR10	Triplet	0.720	0.140	—	0 : 0 : 1	11.2
ZnPc–NR8	Triplet	0.720	0.140	—	0 : 0 : 1	8.9
ZnPc–NR6	Quartet	0.205	0.035	0.19	0 : 1 : 1 : 0	6.8
ZnPc–NR5[b]	Quartet	0.190	0.035	0.17	0 : 1 : 1 : 0	6.1
ZnPc–NR4	Quartet	0.165	0.035	0.15	0 : 1 : 1 : 0	5.6

[a] Sublevel population ratios denote $P_x : P_y : P_z$ and $P_{+3/2'} : P_{+1/2'} : P_{-1/2'} : P_{-3/2'}$ for the triplet and quartet states, respectively. [b] From ref. 14(*b*).

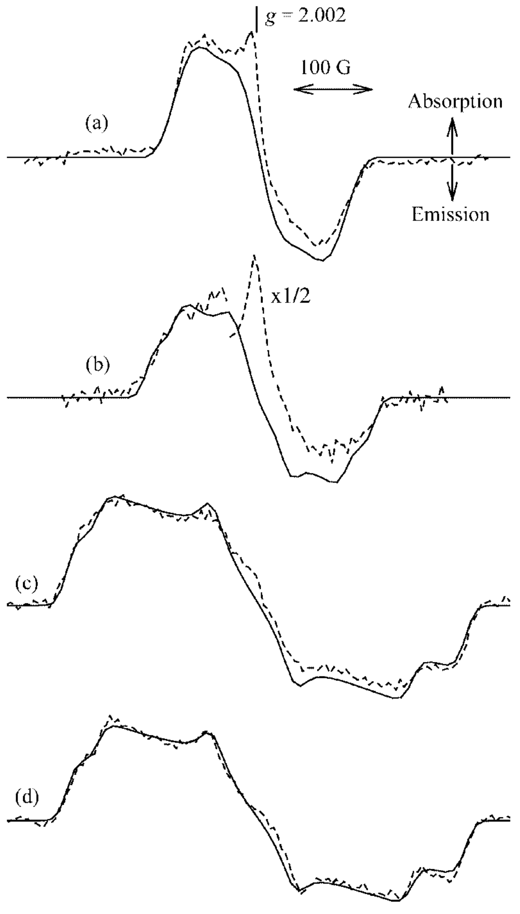

Fig. 2 TREPR spectra (- - -) of ZnPc–NR4 (a), ZnPc–NR6 (b), ZnPc–NR8 (c) and ZnPc–NR10 (d) together with simulations (—— a–d). All spectra were observed at 20 K and 0.8–1.4 μs after laser excitation.

EPR parameters of ZnPc–py are identical with those of ZnPc–bua, indicating that the EPR parameters do not reflect the difference between pyridine and amine.

TREPR spectra of ZnPc coordinated by NRX (X = 4, 6, 8 and 10) are shown in Fig. 2 (broken lines). These spectra can be divided into two groups. The TREPR spectra of the first group, comprising the ZnPc–NR8 and ZnPc–NR10 complexes, are reproduced using the same parameters as ZnPc–py (Table 1), and show that the T_1 ZnPc is not influenced by the nitroxide radical of the NR8 or NR10 ligand. In contrast, the TREPR spectra of ZnPc–NR4 and ZnPc–NR6 are obviously different from those of the NR8 and NR10 complexes, implying a significant interaction between the T_1 ZnPc and doublet nitroxide. These spectra show an *AAE* polarization pattern. The central *A* peaks (g = 2.006 ± 0.0015) are assigned to the doublet ground state by comparison with the steady state EPR spectra (the peak position is at g = 2.006 ± 0.0015). On the other hand, the outer *A*/*E* signals are considered to originate from the Q_1 state constituted by the T_1 ZnPc and doublet nitroxide radical, and are reproduced using the parameters summarized in Table 1. In order to clearly assign these *A*/*E* signals, calculations of zfs parameter D values in the Q_1 state, $D(Q_1)$, were carried out.[13,14] $D(Q_1)$ was calculated by diagonalizing the matrix $\boldsymbol{D}(Q_1)$ [eqn. (1)].[9]

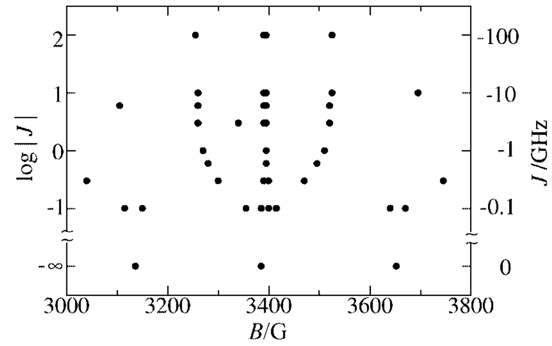

Fig. 3 Resonance magnetic fields calculated for $B//z$ and ν = 9.5 GHz. The resonance magnetic fields were calculated using parameters described in the text.

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

Here, $\boldsymbol{D}(T_1)$ and $\boldsymbol{D}(RT_1)$ denote the matrix of the excited triplet and magnetic dipole–dipole interactions between the T_1 ZnPc and nitroxide radical, respectively. $\boldsymbol{D}(T_1)$ was evaluated from the TREPR spectrum of ZnPc–bua, while $\boldsymbol{D}(RT_1)$ was calculated under a point charge approximation.[13,14,20,21] The calculated $D(Q_1)$ values are summarized in Table 1, and are similar to those obtained experimentally. Therefore, the *A*/*E* signals are assigned to the Q_1 state. It is found by comparison with the previous study of ZnPc–NR5 that the $D(Q_1)$ value decreases in the order ZnPc–NR6 (0.205 GHz) > ZnPc–NR5 (0.190 GHz) > ZnPc–NR4 (0.165 GHz).[14b] In these complexes, $D(T_1) > 0$, $D(RT_1) < 0$, and $|D(T_1)| > |D(RT_1)|$. Since the $D(T_1)$ values of these complexes are similar, the decrease in the $D(Q_1)$ values indicates that the $|D(RT_1)|$ value increases in the order ZnPc–NR6 < ZnPc–NR5 < ZnPc–NR4.[13] This tendency is consistent with the number of bonds X from zinc to the nitroxide nitrogen. The *A*/*E* polarization pattern of the Q_1 state is reproduced by selective ISC to the $|Q_1, \pm 1/2'\rangle$ sublevels. This selectivity is reasonably explained by SOC of d_π orbitals on the zinc ion between the excited doublet states and $|Q_1, \pm 1/2'\rangle$ sublevels.[13,14]

It is found that the TREPR spectra of ZnPc–NR8 and ZnPc–NR10 are very similar to that of ZnPc–py. These similarities show that the electron exchange interaction between the T_1 ZnPc and doublet nitroxide is negligibly small for the NR8 and NR10 complexes. In contrast, the TREPR spectra of the NR4, NR5 and NR6 complexes are assigned to the Q_1 state, indicating a significant interaction between the T_1 ZnPc and doublet nitroxide radical. To evaluate the T_1 and Q_1 TREPR spectra, the J dependence of resonance magnetic fields (Fig. 3) was calculated using the spin Hamiltonian of the radical-triplet system [eqn. (2)].[10]

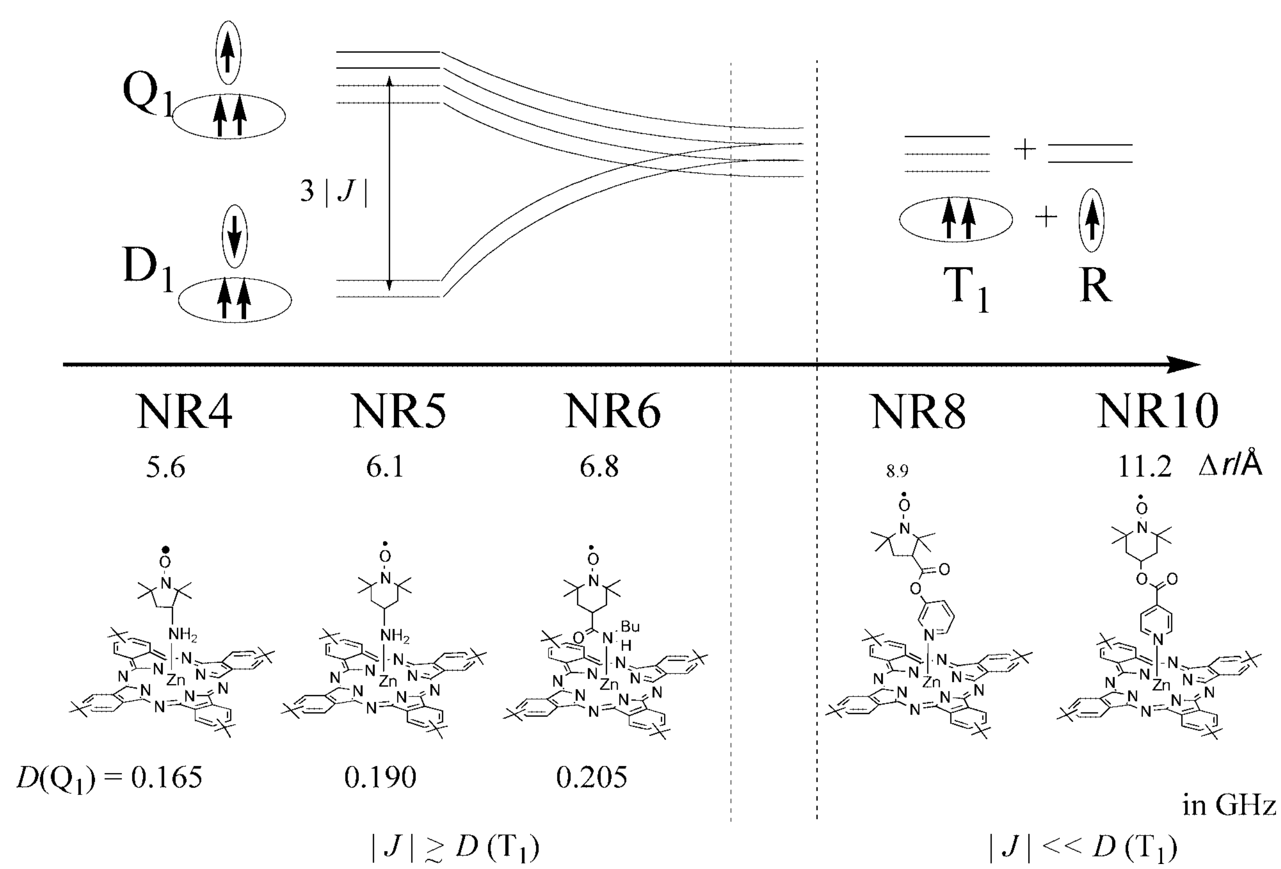

Fig. 4 Summary of magnetic interactions in the ZnPc–NRX system.

$$H=\sum_i \beta g^{(i)}\boldsymbol{B}\boldsymbol{S}^{(i)}+(1/3)\sum_i\sum_{i<j}\boldsymbol{S}^{(ij)}\boldsymbol{D}^{(ij)}\boldsymbol{S}^{(ij)}-2J\,\boldsymbol{S}^{(12)}\boldsymbol{S}^{(3)} \qquad (2)$$

$$i = 1, 2 \text{ or } 3, j = 2 \text{ or } 3$$

Here, β is the Bohr magneton, $\boldsymbol{S}^{(i)}$ is the electron spin operator of electron i, $\boldsymbol{g}^{(i)}$ is the g tensor of electron i, $\boldsymbol{B}$ is the external static magnetic field, and $\boldsymbol{D}^{(ij)}$ is the tensor of magnetic dipole–dipole interaction between electrons i and j.[22] In these calculations, we used $D(T_1) = 0.720$ GHz, $E(T_1) = 0.105$ GHz,[23] $D(RT_1) = -0.160$ GHz, $g(T_1) = 2.000$, $g(R) = 2.006$, $v = 9.5$ GHz, and $B//z$. Important features of the resonance magnetic fields in Fig. 3 are listed as follows. For $J = -100$ GHz, only four typical transitions (|Q,±3/2> ⇔ |Q,±1/2>, |Q,+1/2> ⇔ |Q,−1/2> and |D,+1/2> ⇔ |D,−1/2>) are seen, since the quartet state is well separated from the doublet state. In case of $J = -10$ to -3 GHz, transitions between the doublet and quartet states, which are originally forbidden, appear in addition to four typical transitions. When $J = -0.3$ to -0.1 GHz, many transitions, which are obviously different from the Q_1 TREPR spectra observed for the NR4, NR5 and NR6 complexes, can be seen. Without the electron exchange interaction ($J = 0$), the resonance magnetic fields of the T_1 ZnPc and doublet nitroxide are seen. That is, the resonance magnetic fields correspond to the Q_1 TREPR spectra only when $|J| > D(T_1)$ (0.720 GHz). Therefore, it is found that the $|J|$ values of the NR4, NR5 and NR6 complexes are larger at least than the $D(T_1)$ value, while those of the NR8 and NR10 complexes are much smaller than the $D(T_1)$ value.

To clarify the relationship between the structure and magnetic interactions, optimum structures were calculated using a PM3 Hamiltonian.[24] In the calculated structures, the zinc ion lies 0.44–0.47 Å away from the plane composed of four isoindole nitrogen atoms of the Pc ligand. This displacement of the zinc ion calculated is similar to that (0.48 Å) evaluated from the X-ray analysis of (phthalocyaninato)zinc coordinated by *n*-hexylamine.[20c] Further, the distance between zinc and ligating nitrogen of the nitroxide ligand is calculated to be 2.1–2.3 Å, and is similar to that (2.18 Å) of the X-ray analysis. These comparisons suggest that these optimum structures are reasonable. From the optimum structures, the distance between zinc and nitroxide nitrogen atoms, Δr, is evaluated as 5.6, 6.1, 6.8, 8.9 and 11.2 Å for the NR4, NR5, NR6, NR8 and NR10 complexes, respectively. The number of bonds X, distance Δr, J and $D(Q_1)$ values are summarized in Fig. 4. The J and $D(Q_1)$ values are well correlated with the number of bonds X and distance Δr, and the conditions for forming the excited quartet state have been evaluated experimentally.

Conclusion

In this report, we have studied the magnetic interactions between the T_1 ZnPc and doublet nitroxide radical by TREPR. Five ZnPc complexes with different numbers of bonds from zinc to nitroxide nitrogen (X) have been investigated. In the optimum structures calculated, the number of bonds X is well correlated with the distance Δr. The TREPR spectra of ZnPc–NR8 and ZnPc–NR10 are almost identical with that of ZnPc–py, indicating that these $|J|$ values are much smaller than the $D(T_1)$ value (0.720 GHz). On the other hand, ZnPc–NR4, ZnPc–NR5 and ZnPc–NR6 form the Q_1 state. Calculations of resonance magnetic fields indicate that the $|J|$ values of the NR4, NR5 and NR6 complexes are larger at least than the $D(T_1)$ value. The $|J|$ and $D(Q_1)$ values are well correlated with the number of bonds X and distance Δr. This EPR study is useful for understanding the photophysical and photochemical properties of chromophores.

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21 Because of the degeneracy in the T_1 region of ZnPc, $D(Q_1)$ was evaluated by averaging $D(Q_1)$ values calculated for the $(a_{1u}e_{gx})$ and $(a_{1u}e_{gy})$ configurations,[14c] where the a_{1u} and e_g denote the HOMO and LUMO of ZnPc, respectively.

22 $D^{(12)} = D(T_1)$, $D^{(23)} + D^{(13)} = D(RT_1)$, $E^{(12)} = E(T_1)$, $E^{(23)} = E^{(13)} = 0$, $(g^{(1)} + g^{(2)})/2 = g(T_1)$, and $g^{(3)} = g(R)$. Here, $g(T_1)$ and $g(R)$ denote the g values of the T_1 ZnPc and nitroxide radical, respectively.

23 $E(T_1)$ was evaluated as follows: $E(Q_1)$ values of the NR4, NR5 and NR6 complexes are 0.035 GHz. Since $E(T_1) = 3E(Q_1)$, this was calculated as 0.105 GHz for the NR4, NR5 and NR6 complexes.

24 PM3 calculations were carried out by means of the *program Hyper Chem R. 5. 1*, Hypercube Inc., Florida, 1998.