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ARTICLES

Triplet−Triplet Intramolecular Energy Transfer in a Covalently Linked Copper(II) Porphyrin−Free Base Porphyrin Hybrid Dimer: A Time-Resolved ESR Study

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Triplet−triplet intramolecular energy transfer in a covalently linked copper(II) porphyrin−free base porphyrin hybrid dimer was examined by time-resolved (TR) ESR measurements of the lowest excited triplet (T_1) state of the free base porphyrin component after laser pulse excitation at 532 nm. The TRESR spectra of the free base moiety in the hybrid dimer in toluene glass at 77 K exhibit a spin polarization pattern different from that for the free base porphyrin monomer. The observed pattern for the dimer cannot be explained by any intersystem crossing (ISC) process, and it is ascribed to intramolecular energy transfer that takes place from the copper porphyrin part to the free base counterpart between the triplet manifolds. On the other hand, the TRESR spectrum in 2-methyltetrahydrofuran (2-MTHF) glass, where the energy transfer is prohibited by the fast deactivation of the excited copper porphyrin, shows the same spin polarization pattern as that of the free base porphyrin monomer. Therefore, the copper porphyrin does not affect spin selectivity of ISC in the free base counterpart. The analysis of the TRESR spectrum in toluene suggests that the energy transfer produces the spin population dominantly into T_{+1} and T_{-1} high-field spin sublevels of the T_1 state of the free base porphyrin. In addition to the ESR signals of the T_1 state showing the same fine structure as that for the free base monomer, a moderately intense and narrow emissive band with a larger decay rate was observed at around 324 mT in toluene while in 2-MTHF this band is absent. This emission band may arise from a dimer having a different conformation in which the two porphyrin halves are closer to each other. This kind of conformation gives rise to the strong interaction between the electron spins in the ground state of the copper(II) porphyrin and in the T_1 state of the free base porphyrin.

Introduction

Energy transfer processes in porphyrin dimers have been well studied with relevance to the initial stage of photosynthetic reaction and photoharvesting systems.[1−10] It is very important by itself to investigate energy transfer processes systematically for the better understanding of their mechanism. Porphyrin dimers are suitable for exploration of intramolecular processes, and a whole variety of the linkages between the two porphyrins are advantageous for the systematic investigation. Especially in the porphyrin hybrid dimers having two different central metal ions, identification of the energy acceptor and the donor can be easily done in contrast with the dimers consisting of two equivalent porphyrins. In most hybrid dimers, the energy difference of the excited states of the two porphyrin halves is sufficiently large to ignore exciton hopping and charge resonance in the excited species, while such interactions are rather important in homodimers.[11−13]

Generally, the lowest excited singlet (S_1) and triplet (T_1) states of metalloporphyrins have higher energy levels than those of the corresponding free base porphyrins, respectively.[14] Thus, in these hybrid dimers with nonequivalent components, the metalloporphyrin part can act as an energy donor while the free base porphyrin part is the energy acceptor during the excitation energy transfer process. It is well-known that singlet−singlet energy transfer takes place efficiently in zinc(II) porphyrin−free base porphyrin hybrid dimers.[1−4] In this case, energy transfer from the S_1 state of the zinc porphyrin to that of the free base porphyrin is much faster than the other relaxation processes of the S_1 state of the zinc porphyrin.

Triplet−triplet intramolecular energy transfer in a covalently linked copper(II) porphyrin−free base porphyrin hybrid dimer was examined by means of transient absorption measurements.[5] In copper porphyrins, interaction of an unpaired d electron of the copper ion with the porphyrin π electrons makes porphyrin triplet states split into trip-doublet (^2T) and trip-quartet (^4T) states by several hundred cm^{-1} [15] and accelerates the intersystem crossing (ISC) from the porphyrin excited singlet (as a whole system, sing-doublet, $^2S_1$) state to the excited triplet manifolds ($^2T_1$ and $^4T_1$).[16−19] This fast ISC process can compete with the energy transfer process from the singlet state, and triplet−triplet energy transfer is expected. The transient absorption measurements showed that the generated yield of the T_1 state of the free base moiety in the hybrid dimer was 3 times larger than that of the free base porphyrin monomer, and an efficient triplet−triplet energy transfer from the copper porphyrin to the free base porphyrin partner was suggested.[5] However, there was no direct evidence for triplet−triplet energy transfer because the rise of the transient absorption of the energy acceptor could not be observed as a result of the fact that the T−T absorption spectra of the two porphyrins overlap.

In the case of singlet−singlet energy transfer, the fluorescence

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excitation spectra of the energy acceptor can prove that the energy transfer occurs between the excited singlet−singlet states. This method, however, is not useful for triplet−triplet energy transfer because the transition dipole moment between the triplet state and the ground state is negligible in most cases. On the other hand, time-resolved (TR) ESR spectroscopy can provide static and dynamic information on the excited triplet state of molecules; the zero-field splitting (ZFS) constants stand for the electronic structure of the excited triplet state, while spin polarization patterns observed in TRESR spectra represent the relative population ratio of the triplet spin sublevels. Since the selection rule of spin population for the triplet−triplet energy transfer should be different from that for the ISC, it is expected that TRESR spectra clearly indicate the difference of pathways to the specific triplet state.[20−22] Moreover, analysis of the spin polarization pattern will give information on the mechanism of the triplet−triplet energy transfer in terms of spin polarization transfer, which reflects the interaction between the donor and the acceptor.

In this work, we present TRESR spectra of the covalently linked copper porphyrin−free base porphyrin hybrid dimer just after the intramolecular energy transfer and show direct evidence of the triplet−triplet energy transfer. Furthermore, on the basis of the simulation of the TRESR spectrum of the dimer, we will discuss the spin selectivity of the energy transfer in the spin sublevels.

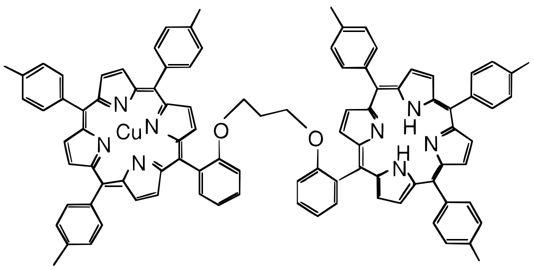
Experimental Section

Materials. The $-(CH_2)_3-$ covalently linked dimer of copper(II) porphyrin−free base porphyrin ($Cu-C_3-H_2$), [5-[2-[3-[2-[10,15,20-tris(4-methylphenyl)-21*H*,23*H*-porphyrin-5-yl]-phenoxy]propoxy]phenyl]-10,15,20-tris(4-methylphenyl)porphyrinato-N^{21},N^{22},N^{23},N^{24}]copper(II) was prepared and purified as described previously.[5] Monomers as impurities were separated by the column chromatography of styrene−divinylbenzene twice, and further purification was carried out according to the literature. The compound was identified by elemental analysis, MASS spectroscopy (FAB-MASS), UV−vis absorption spectra, and the fluorescence quantum yield. The analogous method was used for the preparation of the zinc(II) porphyrin−free base porphyrin hybrid dimer ($Zn-C_3-H_2$). Monomers are also prepared and purified following the previous method.[5]

Measurements. TRESR measurements were carried out with a JEOL RE1X ESR spectrometer equipped with a fast preamplifier without field modulation. Transient ESR signals were transferred to a personal computer NEC 9801FA via a transient memory Kawasaki Electronica Model M-50E after pulse excitation by the second harmonic of a Nd:YAG laser Spectron 401 (532 nm, 10 ns). The transient trace for the EPR signals at each magnetic field was accumulated on the personal computer, and a full set of data were collected over chosen magnetic fields. TRESR spectra were obtained by the summation of the data in the relevant time window at each magnetic field. The base line spectra, which correspond to the spectra before the laser pulse excitation, were subtracted from the raw spectra calculated as above. The magnetic field was calculated from the sweeping voltage, which controls the sweep of the magnetic field from the center magnetic field, and this voltage was detected by a Yokogawa digital multimeter Model 7561 combined to the computer. The magnetic field thus obtained was calibrated by using an Echo Electronics magnetic field meter Model EFM-2000AX. Microwave frequencies were measured with an Echo Electronics EMC-14 microwave counter. Emission spectra at 77 K were measured on a Hitachi 850 spectrophotometer.

Sample solutions were sealed after degassing by freeze−pump−thaw cycles and were equipped in a quartz Dewar at 77 K. Toluene used for solvents was shaken with sulfuric acid after simple distillation, neutralized with dilute aqueous $NaHCO_3$ solution, and then washed with water. After drying on $CaCl_2$, it was distilled again on CaH_2. 2-Methyltetrahydrofuran (2-MTHF) was purified by shaking with 10% aqueous NaOH solution and washing with water. Leaving it on $MgSO_4$ overnight, it was distilled on $LiAlH_4$.

a) structure of Cu-C3-H2



b) energy diagram

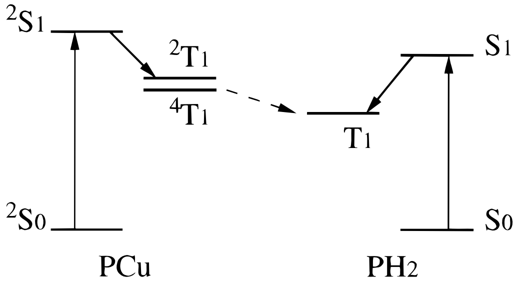


Figure 1. Structure of the covalently linked copper(II) porphyrin−free base porphyrin hybrid dimer ($Cu-C_3-H_2$) and energy diagram of the copper(II) porphyrin and the free base porphyrin.

Results and Discussion

Figure 1 shows the structure of the hybrid dimer ($Cu-C_3-H_2$) and the energy diagrams of copper(II) tetratolylporphin (TTPCu) and free base tetratolylporphin ($TTPH_2$). The T_1 state of the free base porphyrin is lower in energy than the lowest excited triplet manifolds of the copper porphyrin.[19,23] The absorption spectrum of the hybrid dimer in the Q band ($S_1 \leftarrow S_0$) at room temperature corresponds to the superposition of those of monomers in the concentration range between 2×10^{-5} and 5×10^{-4} M, and the transition to the S_1 state takes place independently at each moiety in the dimer.[5] Irradiation at 532 nm, which was used for TRESR measurements, produces the $^2S_1$ state of the copper porphyrin part, about 3 times more than the S_1 state of the free base porphyrin part.

Free base porphyrins exhibit fluorescence from the S_1 state. Figure 2 shows the emission spectra of (a) $Cu-C_3-H_2$ and (b) a 1:1 mixture of $TTPH_2$ and TTPCu in toluene glass at 77 K. The dotted lines show the spectrum of $TTPH_2$ alone, and its intensity was normalized to be the same as that of the mixture or the dimer at the (0,0) band of the fluorescence both in parts a and b. In the mixture, broad emission was observed to the red of the fluorescence, and this broad emission is assigned to the phosphorescence from the copper porphyrin. In the case of $Cu-C_3-H_2$, the fluorescence from the free base part was also observed but the emission from the copper porphyrin is considerably weaker than that in the mixture. Since the fluorescence excitation spectrum in the dimer corresponds to the absorption spectrum of the free base porphyrin monomer but not to that of the dimer, the quenching of the phosphorescence from the copper porphyrin is not due to the singlet (sing-doublet)-to-singlet energy transfer. The fluorescence quantum

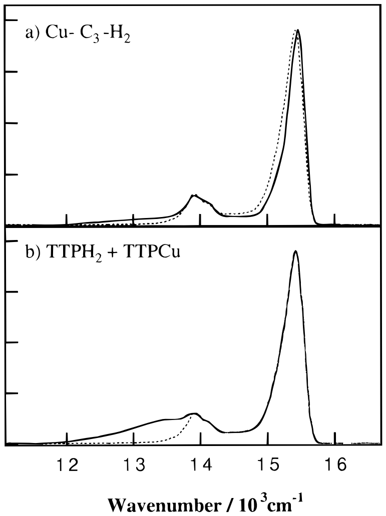


Figure 2. Emission spectra of (a) Cu−C$_3$−H$_2$ (−) and (b) a 1:1 mixture of TTPH$_2$ and TTPCu (−) at 77 K in toluene excited at 540 nm, where it is the maximum of the absorption spectrum of TTPCu. The dotted lines in parts a and b show the emission from TTPH$_2$ alone, and its intensities were normalized (see text). The sample concentrations are ca. 5 × 10^{-6} M.

yield of the hybrid dimer at room temperature is reported to be ca. one-fifth that of the monomer because of the fast ISC within the free base moiety.[5] Assuming that the relative quantum yield of the fluorescence in the dimer at 77 K is the same as that at room temperature, the yield of the emission from the copper porphyrin in the dimer is less than one-tenth that of the mixture. This clearly indicates that the lowest excited triplet manifolds ($^2T_1$ and $^4T_1$) of the copper porphyrin are significantly quenched in the dimer and suggests evidence for energy transfer to the free base part.

Figure 3 shows the TRESR spectra of (a) TTPH$_2$ and its simulation, (b) TTPCu, and (c) a 1:1 mixture of TTPH$_2$ and TTPCu. The spectra were obtained by accumulation for 1−2 μs after the 532 nm laser pulse irradiation in a toluene glass matrix at 77 K. After the excitation to the S$_1$ state, the free base porphyrin relaxes into the T$_1$ state[24] and the observed spectrum in Figure 3a is ascribed to spin polarization in the T$_1$ state generated by ISC. The line shape of the spectrum is well reproduced by the simulation assuming that the relative population ratio into the zero-field triplet sublevels is P_x:P_y:P_z = 0.7:0.3:0 and ZFS constants D and E are 0.0372 cm^{-1} and 0.0079 cm^{-1}, respectively, under the condition of random orientation. The values of the ZFS constants and relative population ratio are similar to those of TPPH$_2$ (tetraphenylporphin) in a toluene−ethanol glass matrix reported in the literature[4] (D = 0.0383 cm^{-1}, E = 0.0080 cm^{-1}, and x, y polarized). It should be noted that the line shape of the TRESR spectrum of TTPH$_2$ does not change with an increase of the delay time, but its intensity decreases.

On the other hand, TRESR measurements of the lowest excited state of TTPCu, $^4T_1$, gave no signal in the magnetic field region up to 500 mT as shown in Figure 3b. The lowest excited trip-quartet state of TTPCu has a longer lifetime of more than 1 ms at 77 K, although the emission decays multiexponentially in rigid matrices.[18,25−27] This value of the lifetime is long enough to detect transient EPR signals. However, the fact that no signal from the copper porphyrin was observed is reasonable because the ZFS constants of the trip-quartet state of the copper porphyrin are too large to detect the ESR transition with X band microwave[28] and the spin relaxation for the trip-quartet state must be very fast compared with our detection limit (0.2 μs). Figure 3c shows that the TRESR spectrum of a 1:1 mixture of TTPH$_2$ and TTPCu is exactly the same as that of the free base monomer. Thus, there is no intermolecular interaction for each porphyrin molecule with this concentration condition (2 × 10^{-4} to 5 × 10^{-4} M).

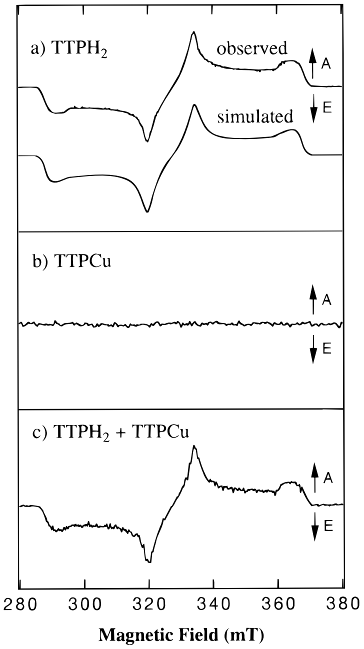


Figure 3. Time-resolved ESR spectra of (a) TTPH$_2$, (b) TTPCu, and (c) a 1:1 mixture of TTPH$_2$ and TTPCu excited at 532 nm (2 mJ) in a toluene glass matrix at 77 K. The concentrations of the samples are (a) 5 × 10^{-4}, (b) 3 × 10^{-4}, and (c) 3 × 10^{-4} M for TTPH$_2$ and 3 × 10^{-4} M for TTPCu. All the spectra were taken in 1−2 μs after pulse excitation with a microwave power of 1 mW. Simulation for the spectrum of TTPH$_2$ was carried out under the following conditions: zero-field splitting constants are D = 0.0372 cm^{-1} and E = 0.0079 cm^{-1}, and the relative population ratio is P_x:P_y:P_z = 0.7:0.3:0. In the figure, A stands for the absorption and E for the emission of the microwave.

Figure 4a shows the TRESR spectra of the copper−free base hybrid dimer in a toluene glass matrix at 77 K at various delay times after the excitation at 532 nm. Clearly, the line shape of the spectrum varies with the delay time. The decay of the emissive signals at around 324 mT is distinct from that of the other signals. The observed TRESR spectra are considered to be a superposition of two kinds of signals: one is represented by the spectrum at 11−12 μs delay time and the other is by the emission band at around 324 mT.[29] Since the line shape and the resonance magnetic field for this emission band are different from those for the typical spectra of triplet states of porphyrins and the signals of this emission band decay independently from the other signals, the origin of this emission band is discussed later. The peaks of the other signals are located very closely at the canonical positions for the T$_1$ state of TTPH$_2$. Therefore, the observed signals that are represented by the spectrum at 11−12 μs delay time can be attributed to the T$_1$ state of the free base porphyrin part in the hybrid dimer. The spin polarization pattern for the dimer, however, is different from that for the monomer. This indicates that the spin selectivity of the T$_1$ sublevels in the hybrid dimer is not the same as that in the free base porphyrin monomer. It is very likely that the intramolecular energy transfer from the copper porphyrin moiety to the free base moiety generates spin polarization in the T$_1$ state of the free base of the dimer.

To exclude the possibility that the observed spin polarization pattern for Cu−C$_3$−H$_2$ arises from perturbed ISC in the presence of the copper porphyrin counterpart, measurements in a 2-MTHF glass matrix were also carried out at 77 K. The obtained

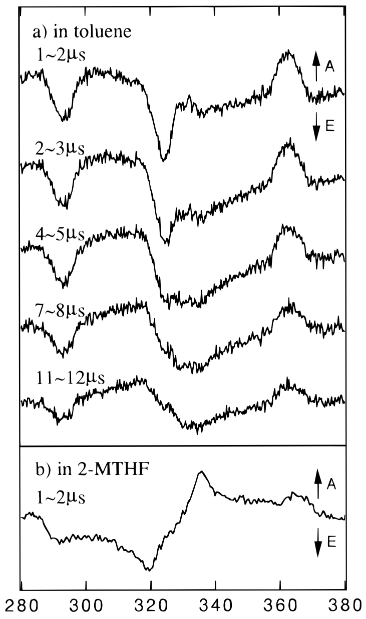


Figure 4. Time-resolved ESR spectra of the hybrid porphyrin dimer $Cu-C_3-H_2$ (a) in toluene glass matrix and (b) in 2-MTHF glass matrix. The concentrations of samples are 4 × 10^{-4} M in both (a) and (b). Delay times are shown, and the other experimental conditions are the same as those in Figure 3.

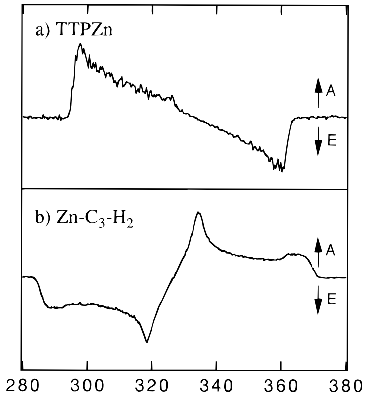


Figure 5. Time-resolved ESR spectra of (a) TTPZn (5 × 10^{-4} M) and (b) zinc(II) porphyrin−free base porphyrin hybrid dimer $Zn-C_3-H_2$ (5 × 10^{-4} M) in toluene glass matrix. The other experimental conditions are the same as those in Figure 3.

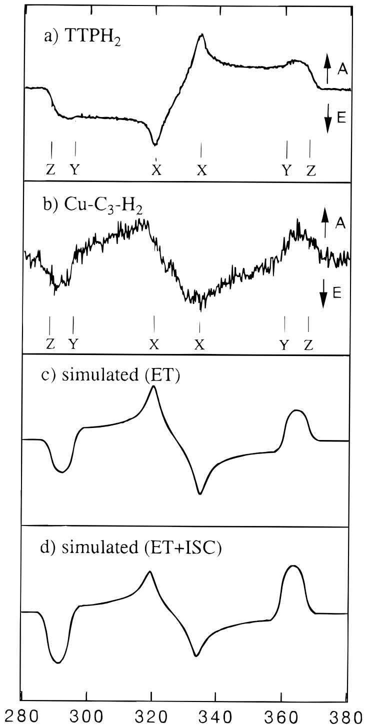


Figure 6. Comparison of time-resolved ESR spectra collected in 11−12 μs after pulse excitation of (a) $TTPH_2$ and (b) $Cu-C_3-H_2$ in toluene glass matrix. In the figure, *X*, *Y*, and *Z* indicate the canonical points. Simulation of the spectrum of the hybrid dimer was carried out considering energy transfer process only (c) and both energy transfer and intersystem crossing processes (d). Conditions used for the simulation are noted in the text.

spectrum, as shown in Figure 4b, is obviously different from that in toluene glass but is quite similar to that of $TTPH_2$. The same results were obtained for the hybrid dimer in a toluene: pyridine = 9:1 glass matrix. In oxygen-containing solvents such as 2-MTHF and coordinating solvents, it is known that the $^{2,4}T_1$ states of copper porphyrins are deactivated promptly to the lower-lying (d,d) and/or CT states.[30,31] Therefore, in a 2-MTHF matrix, intramolecular energy transfer in the hybrid dimer does not take place because of the fast deactivation of the copper $^{2,4}T_1$ states and the T_1 state of the free base part is generated only by ISC from the S_1 state of the free base moiety. The fact that $Cu-C_3-H_2$ in 2-MTHF shows a TRESR spectrum quite similar to that of $TTPH_2$ means that the copper porphyrin part gives no perturbation to the ISC process in the free base porphyrin part in terms of spin selectivity. The observed spin polarization pattern of $Cu-C_3-H_2$ in toluene is due to a process other than ISC. Consequently, it is concluded that the intramolecular energy transfer in $Cu-C_3-H_2$ in toluene takes place from the lowest excited triplet manifolds of the copper porphyrin part to the T_1 state of the free base counterpart.

For some of zinc(II)−free base hybrid porphyrin dimers, singlet−singlet intramolecular energy transfer has been established.[1−4] Figure 5 shows the TRESR spectra of (a) TTPZn and (b) zinc porphyrin−free base porphyrin hybrid dimer ($Zn-C_3-H_2$) in toluene at 77 K. The excitation at 532 nm gives dominantly the S_1 state of the zinc porphyrin in $Zn-C_3-H_2$. The TRESR spectrum of the hybrid dimer is similar to that of the free base porphyrin monomer but different from both that of the zinc porphyrin monomer and the superposition of the spectra of $TTPH_2$ and TTPZn. Since intramolecular energy transfer takes place from the S_1 state of the zinc porphyrin to that of the free base porphyrin,[1−4] the T_1 state of the zinc porphyrin is not produced, but rather that of the free base porphyrin is produced via the ISC within the free base porphyrin moiety. Here, it is noted that the spin polarization pattern in the dimer is the same as that of the monomer caused by ISC when energy transfer takes place between the excited singlet states. This is obviously different from the case for $Cu-C_3-H_2$.

Figure 6 compares the spin polarization patterns for $TTPH_2$ and $Cu-C_3-H_2$ in toluene, 11−12 μs after the pulse excitation. Canonical points are indicated in the figure. The spin polarization at the canonical points of the hybrid dimer is EAA/EEA from low to high magnetic field, while that of the free base monomer is EAE/AEA where A stands for the enhanced absorption and E for the emission of the microwave. As previously mentioned, the spin polarization pattern for the T_1 state of the monomer is well reproduced by a simulation assuming the population of the zero-field triplet sublevels T_x,

T_y, T_z. Since the zero-field interaction of the T_1 state of the free base porphyrin is much weaker than the Zeeman interaction, the triplet sublevels of the free base porphyrin are described as the high-field triplet sublevels T_{+1}, T_0, and T_{-1} in the experimental magnetic field region. For instance, when the molecule lies with the X canonical orientation, T_x serves as T_0 while T_y and T_z are almost equally mixed to form T_{+1} and T_{-1}. Thus, the relative population rate into T_0 is described as P_x while that into T_{+1} or T_{-1} as $(P_y + P_z)/2$. Since the spin polarization at X canonical points in the spectrum of the free base porphyrin monomer is E/A in lower/higher magnetic field, the following relation is derived:

$$P_x > (P_y + P_z)/2 \quad (X \text{ canonical point, E/A})$$

At the other two canonical points, the relations are derived in the same manner:

$$P_y < (P_z + P_x)/2 \quad (Y \text{ canonical point, A/E})$$

$$P_z < (P_x + P_y)/2 \quad (Z \text{ canonical point, E/A})$$

It is clear that the above relations are satisfied with the relative population ratio used for the simulation, $P_x{:}P_y{:}P_z = 0.7{:}0.3{:}0$. Similar consideration of the spin polarization pattern in the spectrum of $Cu-C_3-H_2$ requires the following conditions:

$$P_x < (P_y + P_z)/2 \quad (X \text{ canonical point, A/E})$$

$$P_y < (P_z + P_x)/2 \quad (Y \text{ canonical point, A/E})$$

$$P_z < (P_x + P_y)/2 \quad (Z \text{ canonical point, E/A})$$

Obviously, these relations do not hold at the same time. This means not only that the population of the T_1 state of the free base porphyrin in the hybrid dimer does not take place in the zero-field sublevels but also that any ISC process cannot cause the observed spin polarization pattern in Figure 6b, since ISC is very fast and gives population in the zero-field sublevels.[32]

Instead of population in the zero-field sublevels, the assumption is made that the intramolecular energy transfer populates the high-field sublevels of the T_1 state of the free base moiety. Figure 7 presents the energy diagram of the triplet sublevels in the external magnetic field. At each canonical point, the following relation is required:

$$P_0 < P_{+1}, P_{-1} \quad (X, Y, Z \text{ canonical points})$$

where P_{+1}, P_0, and P_{-1} represent the relative population ratio of the high-field triplet sublevels T_{+1}, T_0, and T_{-1}, respectively. This suggests that the intramolecular energy transfer takes place predominantly into the highest and the lowest high-field sublevels of the T_1 state of the free base porphyrin in the dimer. Based on this feature, a simulation was carried out using the ZFS constants for the T_1 state of $TTPH_2$ and the relative population ratio of the high-field triplet sublevels, $(P_{+1} - P_0){:}(P_{-1} - P_0) = 0.5{:}0.5$, and the result is shown in Figure 6c. Since the 532 nm excitation also produces the S_1 state of the free base porphyrin part, the observed spectrum in Figure 6b should be a contribution of both energy transfer and ISC processes. Figure 6d shows the simulated spectrum in which ISC is also taken into account, that is, a superposition of the simulated spectrum by energy transfer and that by ISC with an arbitrary ratio. This simulation spectrum reasonably matches the observed TRESR spectrum of the dimer. Accordingly, the spin polarization in the TRESR spectrum of the dimer in toluene is caused by the selective population into T_{+1} and T_{-1} high-field sublevels of the T_1 state of the free base moiety.

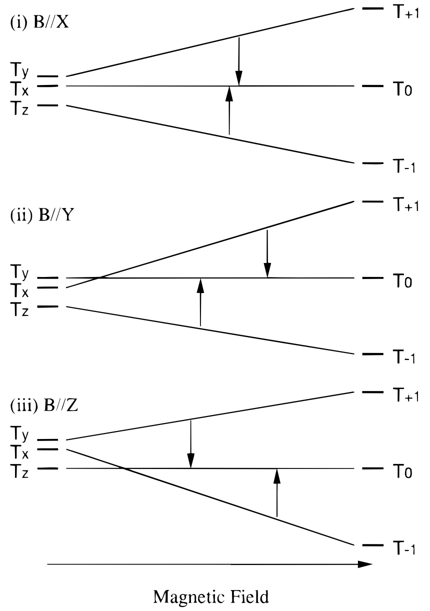


Figure 7. Schematic representation of the spin sublevels of the lowest excited triplet state of the free base porphyrin with canonical orientations. The sublevels are the function of the external magnetic field: zero-field sublevels on the left and high-field sublevels on the right. Arrows represent the ESR transitions at canonical points observed for $Cu-C_3-H_2$ as shown in Figure 6.

It is interesting that the observed TRESR spectrum of $Cu-C_3-H_2$ in toluene has the reversed spectrum pattern from that observed for the T_1 state of bacteriochlorophylls of photosynthetic systems.[33, 34] Their spectra show the spin polarization pattern AEE/AAE from low to high magnetic field. In these photosynthetic bacterium systems, the T_1 state is produced by the recombination of the charge-separated radicals in the singlet state. The recombination takes place through the $S-T_0$ mixing in the radical pair mechanism,[33, 35] which selectively populates the T_0 high-field sublevel of the excited triplet state. This population selectivity is just opposite to what we suggested for $Cu-C_3-H_2$, and it well explains that the spin polarization pattern for the hybrid dimer is totally reversed from that in their spectra.

There may be a possibility that the selective depopulation from the T_0 state causes a polarization pattern similar to the observed one instead of the selective population into the T_{+1} and T_{-1} sublevels. In this case, the spectral pattern from the triplet state of the free base moiety should depend on the delay time because the relative population ratio in the triplet sublevels must change with increasing delay time because of the selective depopulation. Otherwise, the depopulation must be very fast compared with the experimental time scale. The former case is ruled out, since the spectral pattern for the triplet component does not change as shown in Figure 4. In the latter case, the depopulation from the T_0 sublevel should increase the absolute population difference between $T_{+1}$and T_0 as well as that of T_{-1} and T_0 sublevels. The larger population differences would yield more intense signals of the EPR transitions. The observed TRESR spectra of the dimer in toluene, however, show rather poor *S*/*N* ratios even compared with those in 2-MTHF where the ISC is the only process to produce the triplet state, although it is difficult to discuss the absolute intensities of TRESR spectra. Therefore, the selective depopulation from the T_0 sublevel is not suitable for interpreting the obtained spectra.

Whether energy transfer occurs in the zero-field spin sublevels[21] or in the high-field spin sublevels[20] mainly depends on the energy transfer rate. The selective population into the T_{+1} and T_{-1} high-field sublevels suggests that this intramolecular energy transfer may not be very fast, since it takes place after the triplet high-field sublevels are formed by the Zeeman interaction. In fact, decay profiles of the T−T absorption spectra at room temperature show a trace of the lowest excited state of the copper porphyrin moiety in nanosecond measurements, although the rise of the generation of the free base part could not be observed.

The overpopulation in the T_{+1} and T_{-1} sublevels results from either conservation of spin polarization of the $^4T_1$ state of the copper porphyrin or larger energy transfer rates to the T_{+1} and T_{-1} sublevels of the free base porphyrin. Since relaxation of the spin polarization in the $^4T_1$ state of the copper porphyrin should be fast as mentioned previously and since this energy transfer is rather slow, the energy transfer may occur after the establishment of thermal spin population in the $^4T_1$ state of the copper porphyrin. If this is the case, the $^4T_1$ state of the copper porphyrin should have a larger interaction with T_{+1} and T_{-1} sublevels of the free base porphyrin than that with the T_0 sublevel. It is well-known that the ISC ratios to the T_1 state in the metalloporphyrins strongly depend on the central metal ions; ZnTPP gives a z-polarized ISC population ratio while MgTPP gives an in-plane (x, y) polarized ratio.[36] In the present case, perturbation of the copper ion may give rise to larger energy transfer rates into the T_{+1} and T_{-1} sublevels of the free base porphyrin. The experiments on temperature dependence as well as at higher microwave frequencies would give the explicit mechanism for the overpopulation of the T_{+1} and T_{-1} sublevels, and these are in progress.

Finally, the prominent emission band at around 324 mT is discussed, which has a decay rate different from that of the other signals for the T_1 state of the free base porphyrin. Recently, for laser irradiation of a zinc(II) porphyrin−copper(II) porphyrin electrostatically coupled dimer, ZnTTAP−CuTSPP, Hugerat et al. observed broad absorption EPR signals besides the signals for the T_1 state of zinc(II) porphyrin.[37] These absorption signals were tentatively assigned to spin polarization in the ground doublet state of the copper ion caused by irradiation of the zinc porphyrin in the dimer. In contrast with their considerably broad absorption band, the spectral width of the emission in the hybrid dimer $Cu-C_3-H_2$ is rather narrow, and the origin of our prominent band seems different from that of their signals. Despite the difference of the spectral widths, one may think that the signals come from the ground state of the copper ion, which is polarized during the depopulation of the free base triplet levels because the copper ion is the only doublet species in the molecule. However, this possibility is ruled out, since the prominent band decays more quickly than the other signals from the triplet sublevels in the free base porphyrin. If the depopulation of the triplet state in the free base moiety causes the spin polarization in the ground state of the copper ion, the signals should decay at least with the same time constant as that of the triplet signals or slower. An alternative interpretation for the observed signals can be made as a result of the interaction between the T_1 state of the free base porphyrin part and the ground doublet state of the copper porphyrin part in the following way. This hybrid dimer is flexible in terms of structure because of the covalent linkage. Two possible conformations were proposed as representative structures: one is a close conformation and the other is an opened conformation.[38] The existence of two conformers may explain the change of the relative intensities of the two kinds of signals.[29] It is likely that the opened conformer contributes to the ESR signals for the triplet state of the free base porphyrin, while the closed conformer to contributes to the prominent emissive signals due to the strong interaction between the π electrons in the T_1 state of the free base moiety and an unpaired d electron in the copper ion. TRESR measurements for rigidly linked porphyrin hybrid dimers, in which two porphyrins are located rather close to each other, suggest a strong paramagnetic interaction between the two porphyrin;[39] the T_1 state of the free base porphyrin moiety may split into doublet and quartet spin states because of the interaction with the ground doublet state of the copper porphyrin counterpart. This is analogous to the system for RTPM (radical triplet pair mechanism),[40,41] and recently, TRESR measurements on the systems that contain an excited triplet molecule connected to an organic radical suggested the presence of quartet and/or doublet states.[42,43] Here, we recall that in 2-MTHF and pyridine/toluene matrices the prominent emission signals were not observed. It is likely that ligation of the solvent molecule to the copper ion prohibits closer conformation and only the signals from the opened conformation are observed.

Conclusion

The TRESR spectra of the free base porphyrin part in the copper(II)−free base hybrid porphyrin dimer were shown just after the selective excitation of the copper(II) porphyrin moeity at 532 nm. The observed spin polarization pattern strongly suggests that intramolecular energy transfer takes place from the copper(II) part to the free base part between the triplet manifolds. The simulation of the TRESR spectrum of the dimer indicates the selective population into T_{+1} and T_{-1} high-field triplet sublevels of the free base porphyrin part.

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