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A Time-resolved ESR Study on Triplet-Triplet Energy Transfer Processes in a Copper(II)-Free-Base Porphyrin Dimer

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ABSTRACT

Energy transfer from a copper porphyrin moiety to its free-base partner is observed in a copper(II)-free-base hybrid porphyrin dimer. By the measurements of T-T transient absorption spectra in toluene, the triplet yield of the free-base porphyrin was found to be increased in the hybrid dimer compared with that in a monomeric free-base porphyrin. Time-resolved ESR study revealed that this intramolecular energy transfer occurs between the triplets. From the simulation of the TR-ESR spectrum, the mean value of the dihedral angle between the donor and the acceptor is estimated as 30 degrees.

1. INTRODUCTION

Laser flash photolysis, needless to say, is one of the most useful techniques to clarify energy transfer processes. In the case that an energy donor and/or acceptor has electron spin(s), time-resolved ESR spectroscopy can be available. TR-ESR spectroscopy provides information not only on energy transfer processes but also on their mechanism from the view point of spin conservation. TR-ESR studies on triplet-triplet *intermolecular* energy transfer processes have been reported,[1] in which a donor and an acceptor are assumed to be randomly oriented. In this work, we apply this approach to *intramolecular* energy transfer processes of a covalently-linked copper(II)-free-base porphyrin dimer, in which geometry between a donor and an acceptor is partially limited.

The advantage of a hybrid dimer is that an energy donor and an acceptor are distinct. The lowest excited singlet and triplet states of the free-base porphyrin monomer are lower than those of the copper porphyrin in energy,

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respectively. The lifetime of the lowest triplet state of the free-base porphyrin is more than 1 ms in the monomer, which shows intense TR-ESR signals. By the paramagnetic perturbation, intersystem crossing in a copper porphyrin is remarkably accelerated and it seems to prevent singlet-singlet energy transfer to another porphyrin moiety. On the basis of TR-ESR measurements, the pathway of energy transfer process in a copper(II)-free-base hybrid porphyrin dimer is clarified and the dihedral angle of the two porphyrin planes is proposed.

2. EXPERIMENTAL

The hybrid porphyrin dimer of copper (II) and free-base, {5-[2-[3-[2-[10,15,20-tris(4-methylphenyl)-21H,23H-porphyrin-5-yl]phenoxy]-propoxy] phenyl]-10,15,20-tris(4-methylphenyl)-porphyrinato]copper(II)-N^{21},N^{22}, N^{23}, N^{24} (*o,o*-$C_3(TTP)_2CuH_2$: figure1) was synthesized as described previously.[2] Monomer free-base porphyrins were prepared by the literature method and chlorin contamination was oxidized by use of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone. Purification of the porphyrins was carried out by column chromatography and recrystallization.

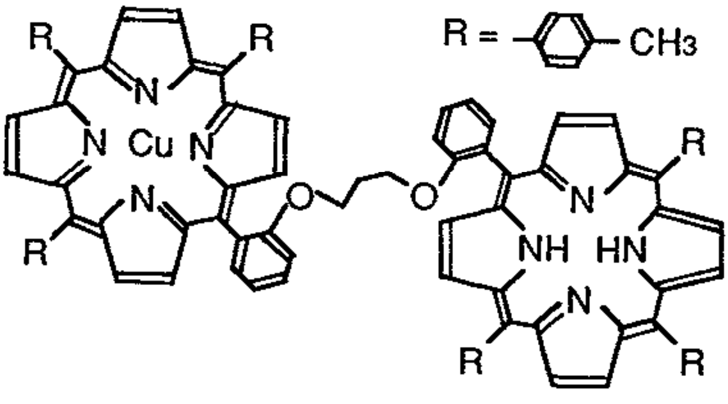

Figure 1 Structure of the copper(II)-free-base porphyrin dimer *o,o*-$C_3(TTP)_2CuH_2$

TR-ESR measurements are carried out without field modulation to improve the time resolution and a wide band amplifier was used for 0.1 μs time resolution. Excited species are generated by irradiation of a second harmonics of a Nd:YAG laser(532nm 8ns). Transient ESR signals were detected by a diode of a conventional X-band ESR spectrometer (JEOL RE1X) and transferred to a transient memory (Kawasaki Electoronika T-50E). The decay curve at each magnetic field was obtained by accumulating signals on a personal computer. TR-ESR spectra were obtained by compiling decay curves in the relevant time area. Sample solutions were sealed after degassing by freeze-pump-thaw cycles and were equipped in a quartz Dewar at 77K.

3.RESULTS AND DISCUSSION

The absorption spectrum of the copper(II)-free-base porphyrin dimer (*o,o*-$C_3(TTP)_2CuH_2$) in the Q band (S_1) corresponds with the superposition of those of the monomers, $TTPH_2$(TTP: 5,10,15,20-tetratolylporphin) and TTPCu. In the B band(S_2), the dimer exhibits a rather broad spectrum compared with that of the 1:1 mixture of the monomers.

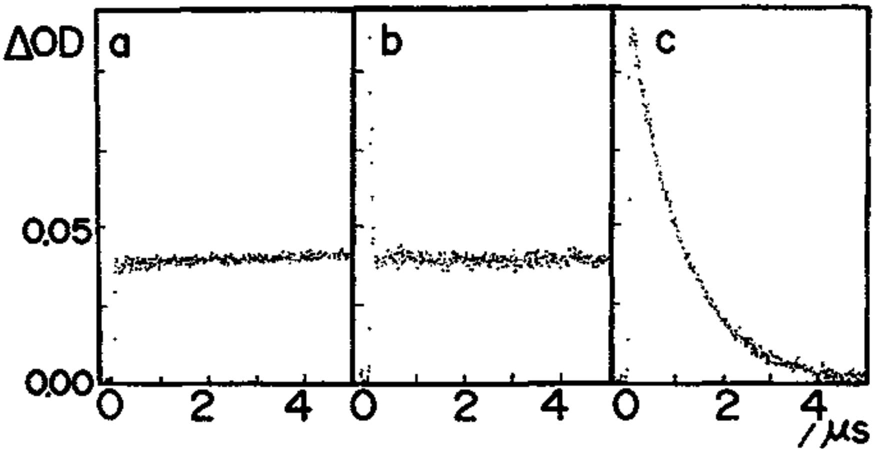

Figure 2 Decay of the T-T transient absorption of a) $TTPH_2$, b) a 1:1 mixture of $TTPH_2$ and TTPCu and c) *o,o*-$C_3(TTP)_2CuH_2$ in toluene.

The free-base monomer, $TTPH_2$, exhibits T-T absorption band with its maximum at around 440 nm, while TTPCu has its T-T absorption maximum at around 480nm. The T-T absorption spectra of the dimer taken with various delay times (10 ns ~ 2 μs) are very similar to those of the free-base monomer, but different from those of TTPCu. Figure 2 shows the T-T absorption decay of $TTPH_2$, the 1:1 mixture of $TTPH_2$ and TTPCu, and the dimer in toluene solution monitored at 446 nm.[2] The concentrations of the free-base moiety are equal in the three solutions. It is noted that the triplet generation yield of the dimer is three times greater than that of the free-base monomer. The intersystem crossing efficiency, that is the triplet generation yield, is about 0.7 in the free-base monomer.[3] Even if the intersystem crossing yield of the dimer equals to unity, the triplet yield is expected at most 1.4 times greater than that of the monomer. This is most likely due to an efficient intramolecular energy transfer from the excited copper porphyrin.

The time-resolved ESR spectrum of the free-base monomer shows an emission-absorption pattern from the lower magnetic field in toluene rigid glass at 77K as shown in figure 3a. The lowest excited triplet state is caused by intersystem crossing from the lowest excited singlet state in the free-base porphyrin. The spectrum in figure 3a can be reproduced by assuming that the initial population of the triplet sublevels as Px:Py:Pz=0:0.3:0.7 and zero-field splitting parameters D, E as 3.7×10^{-2}, 0.8×10^{-2} cm^{-1}, respectively in the random orientation. Figure 3b shows the TR-ESR spectrum of the copper(II)-free-base porphyrin dimer excited at 532 nm, where the excitation gives rise to about twice amount of the excited copper porphyrin than the excited free-base moiety. The signal pattern is different from that of the free-base monomer in figure 3a. This indicates that the lowest triplet state of the free-base moiety in the dimer is generated in a different way from that of the free-base monomer. In the case of the copper monomer porphyrin, any TR-ESR signals are not observed up to 5000 gauss. On the contrary, TR-ESR spectrum of the 1:1 mixture of $TTPH_2$ and TTPCu is exactly the same with that of the free-base monomer and thus the copper porphyrin and the free-base porphyrin does not show any intermolecular interaction in this condition. It leads us to the conclusion that the observed TR-ESR spectrum in the hybrid dimer is due to intramolecular energy transfer which takes place between the triplets from the copper porphyrin moiety to the free-base partner .

In the case of the zinc(II)-free-base porphyrin dimer (o,o-$C_3(TTP)_2ZnH_2$) singlet-singlet energy transfer is established.[4,5] In this dimer, a highly efficient intramolecular energy transfer takes place from the lowest excited singlet state of the zinc(II) porphyrin moiety to that of the free base counterpart. By the excitation at S_1 band, TR-ESR signals were observed. The TR-ESR spectrum of the zinc-free base dimer is the same with that of the free-base monomer but differs from that of zinc(II) porphyrin monomer, which shows an absorption-emission pattern. The lowest excited triplet state of this zinc(II)-free-base dimer, which is localized in the free base moiety, is produced only by intersystem crossing from the lowest excited singlet state of the free-base moiety.

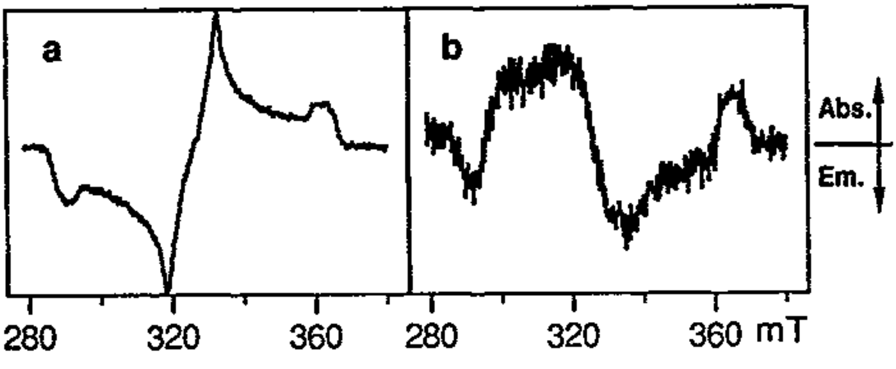

Figure 3 TR-ESR spectra of a) $TTPH_2$ and b) *o,o*-$C_3(TTP)_2CuH_2$ in toluene at 77K.

The lowest excited triplet state of the copper(II)-free-base porphyrin dimer is generated both by energy transfer processes from the triplet manifolds in the copper porphyrin moiety and by intersystem crossing from the lowest excited singlet state of the free-base moiety. To obtain a TR-ESR spectrum only due to the triplet-triplet energy transfer process, the contribution of intersystem crossing, which is to be the same with the spectrum of the free-base monomer, is subtracted. The subtracted spectrum shows an absorption-emission pattern from the lower magnetic field. This ESR spectrum can be simulated according to the following model.

The energy donor, the copper porphyrin, is randomly oriented in the magnetic field. The triplet manifolds in the copper porphyrin are yielded by intersystem crossing from the lowest excited singlet state which is populated by laser irradiation. During the T-T energy transfer process to the free-base porphyrin, spin-polarization of the porphyrin triplet sublevels was conserved between the donor and the acceptor, although the lowest excited triplet manifolds of the copper porphyrin were described as a equilibrium of trip-doublet and trip-quartet states. Flexible structure of the covalently-linked porphyrin dimer results in that the donor and acceptor porphyrins are not in parallel. As the two porphyrin planes make some angle, the acceptor and the donor feel the same laboratory magnetic field in different directions from each other. The direction in which the acceptor feels the magnetic field can be described as a function of that of the donor and the dihedral angle of the two porphyrin planes. Assuming that the dihedral angle between the two porphyrin planes is 30 degrees, the ESR spectrum can be reproduced.

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