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Highly Efficient Triplet−Triplet Intramolecular Energy Transfer and Enhanced Intersystem Crossing in Rigidly Linked Copper(II) Porphyrin−Free Base Porphyrin Hybrid Dimers

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Intramolecular energy transfer as well as excited-state relaxation of gable-type copper(II) porphyrin-free base porphyrin dimers, in which the two halves are linked via a benzene or a naphthalene, was studied by transient absorption and fluorescence spectroscopy. Photoexcitation at 532 nm of the dimer gives rise to transient absorption spectra identical to that of triplet−triplet (T−T) absorption in the free base monomer; however, the absorption intensities in the dimers are more than four times larger than that of the monomer, indicating efficient intramolecular energy transfer from the copper porphyrin to the free base counterpart. Presence of pyridine in the dimer solutions decreases the initial optical densities, while the free base monomer shows no change. The decrease is ascribed to competition between energy transfer via triplet manifolds and quenching by pyridine in the excited trip−quartet and/or trip−doublet states of the copper porphyrin moiety. The analysis of the generated yield of the T_1 free base in the various pyridine/toluene fractions leads to energy transfer rates of sub-nanoseconds. On the basis of the relative absorption intensities as well as the evaluated energy transfer rates, energy transfer efficiency of the dimer in toluene was estimated as almost unity. On the other hand, with the selective excitation of the free base half, the dimers exhibit fluorescence spectra identical to that of the monomer. Fluorescence lifetimes were determined in toluene as 430 ± 30 and 890 ± 30 ps for the benzene-bridged dimer ($Cu-Bz-H_2$) and the naphthalene-bridged dimer ($Cu-Np-H_2$), respectively. Fluorescence intensities of $Cu-Bz-H_2$ and $Cu-Np-H_2$ are $^1/_{28}$ and $^1/_{13}$ of that of the monomer, respectively. Intersystem crossing (ISC) in the free base part is remarkably enhanced in the hybrid dimer. We propose that the interaction between an unpaired electron in the copper(II) and the triplet of the free base via exchange coupling gives rise to the partially allowed character of ISC in the free base half of the hybrid dimers.

1. Introduction

Numbers of porphyrin dimers and their related compounds have been synthesized and extensively studied from the viewpoint of photoinduced intramolecular processes and interaction between the two halves.[1−26] One of the most advantageous aspects of the porphyrin-based system is that a whole variety of the linkages of the dimers enables the systematic investigation in terms of distance and orientation between the two chromophores. This is based on the fact that the nature of each

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porphyrin constituent is not largely affected by the spacer in most of these dimers due to a large π-conjugation. Another point is that the central metal ion of the macrocycle can change excited energies and redox potentials of the ring, and thus it is possible to control the rates of photophysical processes by varying two metal ions. On these grounds, porphyrin hybrid dimers having two different central metal ions serve as excellent models for the studies of intramolecular energy transfer and charge separation.[5−20] This is in contrast with the dimers consisting of two equivalent porphyrins, wherein energy or electron hopping and charge resonance, in turn, appear to be important issues.[21−26]

It is well-established that zinc(II) porphyrin−free base porphyrin hybrid dimers undergo singlet−singlet energy transfer from the S_1 state of the zinc half to the free base.[5−12] In contrast, copper(II)-free base hybrid dimers are expected to undergo triplet−triplet energy transfer from the copper moiety to the free base.[15] This is because photoexcitation into the excited (porphyrin) singlet state of the copper porphyrin half proceeds to fast relaxation to the triplet manifolds[27,28] and the singlet−singlet energy transfer is retarded. The difference in the behaviors between the two types of dimers, i.e., zinc−free base and copper−free base dimers, arises from the fact that the copper ion has an unpaired electron in the d_σ orbital, which interacts with porphyrin π-electrons.[29] Exchange interaction of the metal unpaired electron with π-electrons splits porphyrin triplets into trip−doublet (^{2}T) and trip−quartet (^{4}T) states with an energy gap of several hundred cm^{-1}, while porphyrin singlet states can be described as sing−doublet (^{2}S) states in the copper porphyrin. Herein, symbols ^{2}T, ^{4}T, and ^{2}S have been used for referring to the trip−doublet, trip−quartet, and sing−doublet states, respectively. Partially allowed character of the transition between the $^2S_1$ and $^2T_1$ states results in picosecond rates of intersystem crossing (ISC) within copper porphyrin monomer. It should be noted that copper porphyrins have been studied intensively over the past decades[27−42] to understand the interaction and effects of a metal unpaired electron on the π-electron system. However, in the case of dimers containing paramagnetic ions, relatively little attention has been paid to such systems, although they are expected to exhibit different photophysics from that of diamagnetic complexes.[15−19] The role of the metal unpaired electron has not been well-clarified in terms of the dynamics of the intramolecular processes in such supramolecules.

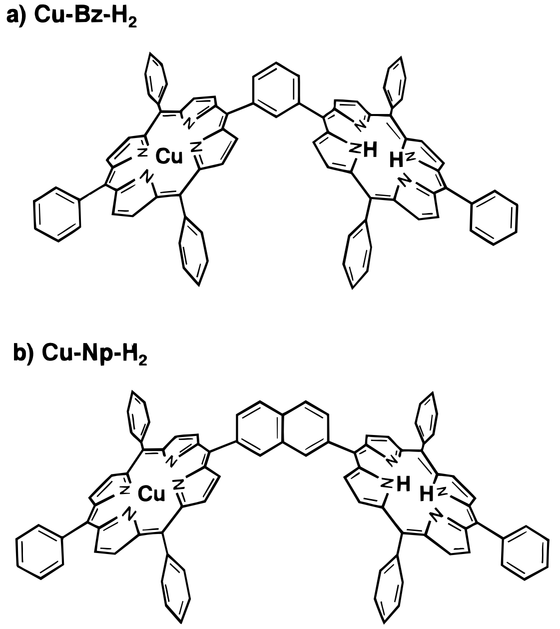

Figure 1. Molecular structures of the copper(II) porphyrin−free base porphyrin dimers.

Previously, we observed triplet−triplet energy transfer in a covalently linked copper porphyrin−free base porphyrin dimer by means of transient absorption measurements[15] and recently extended the previous study by using time-resolved electron paramagnetic resonance.[16] In the latter study, we discussed the mechanism of energy transfer in terms of spin polarization transfer as well as the interaction between the excited triplet state of the free base and an unpaired electron in the copper ground state. However, because of a conformational flexibility of the carbon-chain linkage of this dimer, there are expected to be at least two conformations, thus giving rise to some ambiguity in the analysis of the results. In this context, dimers which have a rigid bridge between the two chromophores are much desired to overcome the above disadvantage.

In the present work, we chose two gable-type copper porphyrin−free base porphyrin hybrid dimers linked by benzene and naphthalene. Figure 1 shows the two dimers, (a) Cu−Bz−H$_2$ (the benzene-bridged dimer) and (b) Cu−Np−H$_2$ (the naphthalene-bridged dimer). In these compounds, the linkage

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itself is not flexible because of the π-conjugated system that spreads over the whole of the spacer part. Moreover, the dihedral angle between the two porphyrin components is expected to be considerably restricted because of stereochemical repulsion between the porphyrin macrocycle and the spacer.[43] This inflexibility limits conformation of the molecules in terms of the donor−acceptor distances and orientations. In these copper−free base porphyrin dimers, we show not only that triplet−triplet energy transfer occurs with an efficiency of approximately unity but also that ISC process within the free base part is significantly affected by the copper counterpart. Differences in these dimers lead to a support for the presented mechanism that can account for the observed energy transfer and the enhancement of the ISC rates on the free base moiety.

2. Experimental Section

Materials. Monomeric free base tetraphenylporphyrin and its copper(II) complex were prepared and purified as described previously.[36]

Free base benzene-bridged porphyrin dimer (1,3-bis(5′-(10′,15′,20′-triphenylporphinyl))benzene) was prepared via the stepwise porphyrin ring closure, according to the method of Tabushi et al.[43] After being purified by column chromatography and recrystallized from dichloromethane/methanol, the final product was identified by elemental analysis, ^{1}H NMR, MS, and UV−vis absorption spectroscopy.

1,3-Bis(5′-(10′,15′,20′-triphenylporphinyl))benzene: Anal. Calcd for $C_{82}H_{54}N_8$ (mol wt 1151.4): C, 85.54; H, 4.73; N, 9.73. Found: C, 85.31; H, 4.70; N, 9.66. FAB MS, *m/z* 1151(M$^+$ + 1). ^{1}H NMR (CDCl$_3$): −2.70 (s, 4H), 7.6−7.9 (m, 18H), 8.1−8.3 (m, 13H), 8.64 (d, J = 8.0 Hz 2H, bridge-phenyl), 8.84 (s, 8H, pyrrole), 8.98 (d, J = 4.6 Hz pyrrole 4H), 9.12 (s, 1H, bridge-phenyl), 9.32 (d, J = 4.4 Hz, 4H pyrrole). $\lambda_{\max}$ (toluene)/nm: 648, 592, 549, 515, 429, 417.

The naphthalene-bridged porphyrin dimer (2,7-bis(5′-(10′,15′,20′-triphenylporphinyl))naphthalene) was synthesized in a method similar to that of the benzene-bridged porphyrin dimer, except for the spacer unit. The preparation of the source aldehyde for the spacer, 2-formyl-7-propionyloxymethylnaphthalene, is outlined below, and detailed procedures of the whole synthesis of this dimer will be described elsewhere. 2,7-Bis(bromomethyl)naphthalene, prepared from 2,7-dimethylnaphthalene by using *N*-bromosuccinimide,[44] was reacted with sodium propionate in propionic acid, thus yielding 2,7-bis(propioxymethyl)naphthalene. After being purified by silica gel column chromatography (dichloromethane/hexane as eluent), this diester was partially hydrolyzed in dioxane containing 0.5% 0.6 N NaOH aqueous solution.[45] A mixture of bis(hydroxymethyl)-, 2-hydroxymethyl-7-propionyloxymethyl-, and bis(propionylmethyl)naphthalene was obtained and separated into the three derivatives by column chromatography (diethyl ether as eluent). 2-Hydroxymethyl-7-propionyloxymethylnaphthalene prepared in this manner was oxidized into 2-formyl-7-propionyloxymethylnaphthalene by using pyridinedichromate.[46]

The first porphyrin ring closure was carried out by the method of Adler et al.,[43,47] while the second ring was condensed by the dilute method of Lindsey et al.[48] For the second condensation, the dilute method provides a higher yield than the method used for the synthesis of the benzene-bridged dimer.[43] The crude product obtained above was purified by column chromatography (silica gel, dichloromethane/hexane; aluminum, dichloromethane) and recrystallized from chloroform/methanol. Characterization data for this new dimer are as follows.

2,7-Bis(5′-(10′,15′,20′-triphenylporphinyl))naphthalene: Anal. Calcd for $C_{86}H_{56}N_8$ (mol wt 1201.4): C, 85.98; H, 4.70; N, 9.33. Found: C, 85.66; H, 4.68; N, 8.97. FAB MS, *m/z* 1201(M$^+$ + 1). ^{1}H NMR (CDCl$_3$): −2.68 (s, 4H), 7.7−7.8 (m, 18H), 8.18−8.27 (m, 12H), 8.52 (d, J = 7.8 Hz 2H, naphthalene), 8.64 (d−d, J = 8.5 Hz 2H, naphthalene), 8.85 (s, 8H, pyrrole), 8.90 (s, 2H, naphthalene), 8.92 (d, J = 5.1 Hz, 4H, pyrrole), 9.07(d, J = 5.1 Hz 4H, pyrrole). $\lambda_{\max}$ (toluene)/nm: 648, 592, 549, 515, 428, 419.

The free base porphyrin homo-dimers were converted into monometalated porphyrin dimers in chloroform by reacting with copper(II) acetate of 80% amounts of the dimer, which corresponds to 40% amounts of the total porphyrin moieties. A mixture of non-copper(II), mono-copper(II), and bis-copper(II) porphyrin dimers was obtained and separated by silica gel column chromatography (CHCl$_3$:hexane = 1:1) twice. During the second chromatography procedure for the portion which mainly contains monometalated species, no contamination of the other derivatives as well as no trace of decomposition could be noticed. Further purification of the mono-copper(II) dimers, namely, copper porphyrin−free base porphyrin hybrid dimers, was carried out by column chromatographies (aluminum and silica gel, dichloromethane) and recrystallized from dichloromethane/ethanol, so as to obtain the final product clean enough for the fluorescence lifetime measurements.

[5-[3-[10,15,20-Triphenyl-21*H*,23*H*-porphin-5-yl]phenyl]-10,15,-20-triphenylporphyrinato]copper(II)−*N*^{21},*N*^{22},*N*^{23},*N*^{24}: Anal. Calcd for $C_{82}H_{52}N_8Cu$ (mol wt 1212.9): C, 81.20; H, 4.32; N, 9.23. Found: C, 81.10; H, 4.46; N, 8.95. FAB-MS, *m/z* 1212(M$^+$ + 1).

[5-[2′-[7′-(10,15,20-Triphenyl-21*H*,23*H*-porphin-5-yl)]naphthyl]-10,15,20-triphenylporphyrinato]copper(II)−*N*^{21},*N*^{22},*N*^{23},*N*^{24}: Anal. Calcd for $C_{86}H_{54}N_8Cu$ (mol wt 1263.0): C, 81.79; H, 4.31; N, 8.87. Found: C, 81.98; H, 4.45; N, 8.64. FAB MS, *m/z* 1262(M$^+$ + 1).

Measurements. Absorption and fluorescence spectra were taken on a Hitachi 330 spectrophotometer and a Hitachi 850 spectrofluorometer, respectively. Fluorescence lifetimes were determined by fitting the emission decay profiles measured by the single-photon-counting method on a Hamamatsu C4790 fluorescence measurement system. Porphyrins were excited at 590 nm (16.9 × 10^3 cm^{-1}), which was prepared from a Laser Photonics LN120C NitroDye laser, consisting of an optional dye laser module (LD2C) and a LN120 UV nitrogen laser. Emission was detected by a streak scope model Hamamatsu C4334 through a Chromex 250IS imaging spectrograph. Delay time between laser pulses and streak scope was controlled by a synchronous delay generator model Hamamatsu C4792-01. Streak image data were transferred to an Apple personal computer model Power Macintosh 7100 through a GPIB interface.

For transient absorption measurements, samples were excited at the second harmonics (532 nm) of a Nd:YAG laser model Spectron 401L (10 Hz, 10 ns). As the monitoring light, a white pulse with a duration time of 10 ms was prepared from a continuous wave Xe lamp and a light chopper, model 5584A (NF Corporation), equipped with two pieces of wings so as to adjust an appropriate time width of the white pulse. The delay time of the laser flash from the rise of the white light was controlled by an electronic delay circuit (Stanford Research, DG535). The transmitted light, i.e., the monitoring light after passing through the sample solution, was detected by a Hamamatsu R928 photomultiplier after dispersed through a Nikon P-250 monochromator. The transient signals were accumulated on a storage oscilloscope, model LeCroy 9450A (350 MHz), and transferred to a personal computer, an NEC model 9801VM through a GPIB interface. The pump/probe, probe-only, and dark signals were measured alternatively using mechanical shutters.[42]

Sample solutions for the measurements of fluorescence were purged with argon gas just before use and sealed. In the case of transient absorption measurements, sample solutions were degassed by a freeze−pump−thaw cycle and sealed in quartz rectangular cuvettes (optical path length, 10 mm). Toluene that was used as a solvent was purified as described previously.[16]

Proton magnetic resonance spectra were recorded on a JEOL EX 270 (270 MHz) or on a JEOL JNM-GSX 500 (500 MHz) in CDCl$_3$

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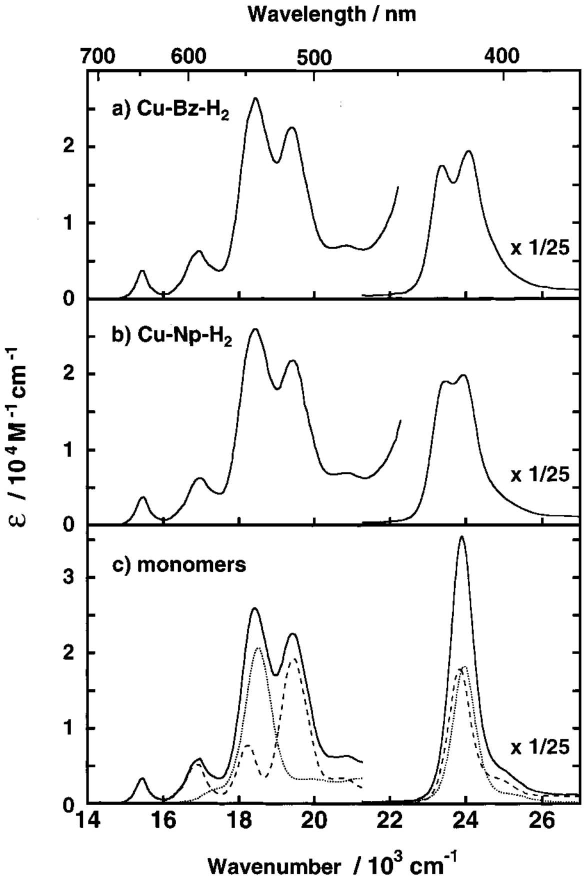

Figure 2. Absorption spectra of (a) Cu−Bz−H$_2$, (b) Cu−Np−H$_2$, and (c) TPPCu (dotted line) and TPPH$_2$ (broken line) in toluene. The solid line spectrum in (c) is generated by adding the spectra of TPPCu and TPPH$_2$.

using tetramethylsilane as an internal standard. FAB-MS spectra were measured on a JMS-AX505HA mass spectrometer (FAB gun, Xe; matrix, m-NBA).[49]

3. Results

Absorption and Fluorescence. Figure 2 shows the absorption spectra of (a) Cu−Bz−H$_2$, (b) Cu−Np−H$_2$, and (c) monomers. In both dimers, the Soret band is split into two bands, while such splitting is not observed either in the spectra of the monomers or in their sum spectrum as shown in part c of Figure 2. A larger splitting is observed in Cu−Bz−H$_2$ than that in Cu−Np−H$_2$: 7 × 10^2 cm^{-1} (peak-to-peak) for Cu−Bz−H$_2$; 5 × 10^2 cm^{-1} for Cu−Np−H$_2$. On the other hand, the absorption spectra in the Q-band of the hybrid dimers are essentially a 1:1 linear combination of those of monomers, TPPH$_2$ and TPPCu. Generally, the lowest excited singlet and triplet states of the free base porphyrin are lower than the corresponding states of metalloporphyrins. Indeed, Q(0,0) absorption band of TPPH$_2$ locates in lower energy region than that of TPPCu.[50]

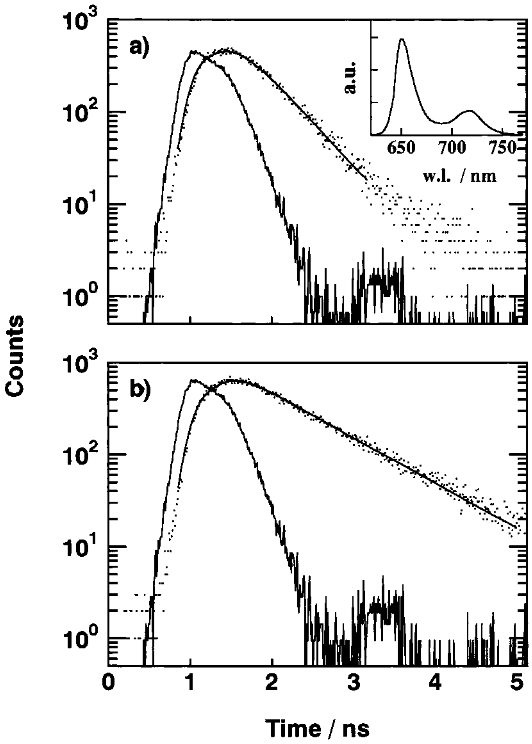

Figure 3. Emission decay profiles of (a) Cu−Bz−H$_2$ and (b) Cu−Np−H$_2$ in toluene at room temperature. Emission data are given by dots, together with the best fitting decay curves (see text for details). The response for the excitation laser is depicted with a solid line and factored by $^1/_3$. Excitation wavelength is 590 nm, while emission is monitored in the wavelength region between 630 and 670 nm. Decay time constants for the fits are (a) 430 ps and (b) 890 ps. Fluorescence spectrum of TPPH$_2$ is shown in the inset.

Monomeric free base porphyrin exhibits intense fluorescence in contrast to copper(II) porphyrin monomer, which does not fluoresce from the lowest excited singlet (sing−doublet) state. In the copper(II)−free base dimers, fluorescence only from the free base is observed. The fluorescence quantum yields in the dimers, however, are remarkably decreased compared with the monomer, without change of the spectral profile. The relative fluorescence intensities to that of the monomer are 0.035 and 0.080 for Cu−Bz−H$_2$ and Cu−Np−H$_2$, respectively. It should be noted that the fluorescence excitation spectra are coincident with the absorption spectra of TPPH$_2$ in the Q-band but not with those of dimers in the both hybrid dimers. This proves that intramolecular energy transfer from the copper(II) part to the free base counterpart does not occur between the excited singlet states.

In correspondence to the decreases of the quantum yields, the fluorescence lifetimes are shorter in the dimers. Figure 3 displays time profiles of the emission together with the fluorescence spectrum in the inset. Solid lines are the best fitting curves, assuming a single-exponential decay. The lifetimes were determined as 430 ± 30 and 890 ± 30 ps for Cu−Bz−H$_2$ and Cu−Np−H$_2$, respectively. Since the lifetime of fluorescence in the free base monomer is 12.5 ns in toluene, the ratios of the lifetimes of these dimers to the monomer are 0.035 and 0.072, for Cu−Bz−H$_2$ and Cu−Np−H$_2$, respectively. These values agree with the intensity ratios of fluorescence quantum yields.

Transient Absorption Spectra. Figure 4 shows transient absorption spectra of the monomers and dimers excited at 532 nm (18.8 × 10^3 cm^{-1}) in toluene as a function of delay times. In TPPH$_2$, the intensity maximum is at ca. 440 nm (22.7 × 10^3 cm^{-1}), while TPPCu exhibits a broad feature centered around 470 nm (21.3 × 10^3 cm^{-1}). The observed spectra in TPPH$_2$ and TPPCu are in good agreement with the triplet−triplet (T−T) absorption spectra reported previously.[15,26] In Figure 4, the

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(49) Yamauchi, N.; Terachi, T.; Eguchi, T.; Kakinuma, K. *Tetrahedron* **1994**, *50*, 4125.

(50) Although there is interaction between the copper unpaired electron and the porphyrin electrons, the excitations are mostly localized in the porphyrin π-system in the $^2S_1$, $^2T_1$, and $^4T_1$ states. Therefore, “singlet” and “triplet”, in terminology, are used on occasion for a better analogy to other metalloporphyrins instead of sing−doublet and a set of trip−doublet and −quartet.

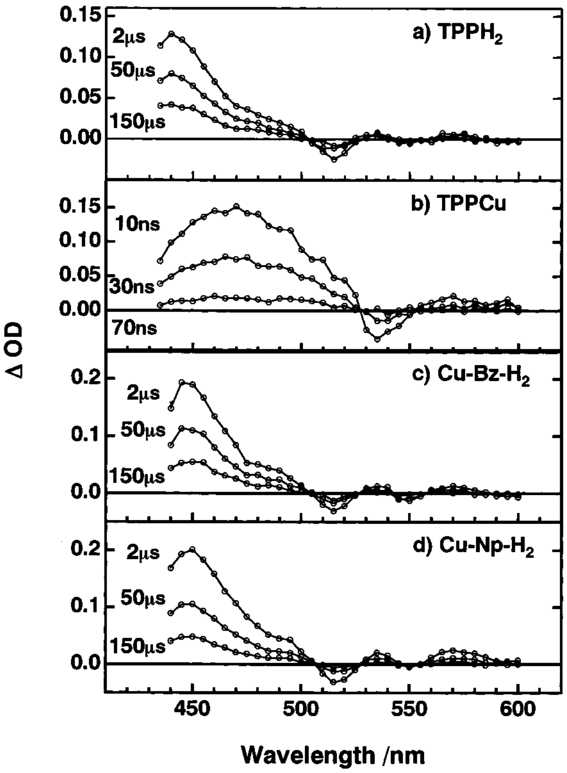

Figure 4. Transient absorption spectra taken with varied delay times after 532 nm laser pulse excitation of (a) TPPH$_2$, (b) TPPCu, (c) Cu−Bz−H$_2$, and (d) Cu−Np−H$_2$ in toluene at room temperature.

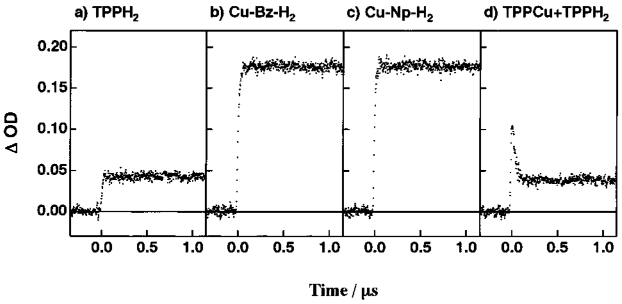

Figure 5. Kinetic profiles for the transient T−T absorption of (a) TPPH$_2$, (b) Cu−Bz−H$_2$, (c) Cu−Np−H$_2$, and (d) a 1:1 mixture of TPPH$_2$ and TPPCu excited at 532 nm, in toluene at room temperature. Monitored wavelength is 450 nm.

transient absorption spectra of Cu−Bz−H$_2$ and Cu−Np−H$_2$ are very similar to the T−T absorption spectrum of TPPH$_2$ but apparently different from that of TPPCu. This indicates that the lowest excited states of the two dimers are localized in the triplet state of the free base part.

The T−T absorption of TPPCu decays with the same time constant as that of the emission from the thermally populated trip−doublet and −quartet states (30 ns at 300 K).[34−37] On the other hand, the intensities in the other three compounds decrease much slower without any change of spectral shape. Even at the earliest time window in our apparatus (ca. 10 ns), the spectral profile is identical to that observed at later delay times. In contrast, the transient absorption spectra of a 1:1 mixture of TPPCu and TPPH$_2$ are the superposition of those of the two monomers (not shown).

Triplet Generated Yields. Figure 5 shows time profiles of transient absorption for TPPH$_2$, Cu−Bz−H$_2$, Cu−Np−H$_2$, and a 1:1 mixture of TPPH$_2$ and TPPCu in 0−1 μs delay time region after laser irradiation at 532 nm (18.8 × 10^3 cm^{-1}). The monitored wavelength of 450 nm (22.2 × 10^3 cm^{-1}) locates near the T−T absorption maximum of the free base. Since each sample for the experiments with Figure 5 has an equal concentration of the free base porphyrin molecules, the initial optical density, i.e., ΔOD at $t = 0$, represents the relative triplet-generated yield of the free base. Apparently, ΔOD at $t = 0$ is largely increased in the dimers compared to the monomer. In both dimers, the relative generated yield of the T$_1$ state is more than four times greater than that in TPPH$_2$, suggesting intramolecular energy transfer from the copper porphyrin to the free base.

Table 1. Relative Initial Optical Densities of Transient Absorption of Copper Porphyrin−Free Base Porphyrin Dimers in Pyridine/Toluene Solution

	ΔOD^D([py])/ΔOD^D(0)	
pyridine (%)	Cu−Bz−H$_2$	Cu−Np−H$_2$
0	“1”	“1”
0.8	0.99	0.97
1.6	0.97	0.93
3.0	0.94	0.85
6.0	0.86	0.74

On the other hand, transient traces of the T−T absorption for the mixture in part d of Figure 5 is superposition of those of the two monomers: the fast component is ascribed to the transient absorption of TPPCu, while the slow component corresponds to that of TPPH$_2$. *Intermolecular* energy transfer was not detected.

Competition of Intramolecular Energy Transfer and Quenching by Pyridine. It is well-known that the excited (porphyrin) triplet manifolds of copper porphyrin are quenched by coordinating solvents such as pyridine. In the presence of such solvent molecules, fast deactivation from the lowest (π,π*) excited state, namely, trip−doublet and trip−quartet states, takes place because of the lowering of (d,d*) and/or CT excited states.[40,41] Transient absorption measurements were carried out in various pyridine/toluene solutions. The band shapes of T−T absorption in the pyridine-containing toluene solutions are the same as those in toluene only, both in the monomer and in the hybrid dimers. However, the initial optical densities of the dimers decrease with an increase of the concentration of pyridine, while it did not in the monomer. This is interpreted in terms of the competition of the relaxation processes from the excited copper moiety, i.e., the intramolecular energy transfer to the free base moiety and the quenching process by pyridine. Table 1 summarizes relative initial optical densities, which were normalized so that the ΔOD in toluene is to be “1” after averaging several series of the measurements.[51]

4. Discussion

Relaxation Processes from the Lowest Excited Singlet State of the Free Base Half. The absorption spectra for the S$_1$−S$_0$ transitions in the hybrid dimers are described as a superposition of those of the two monomers. The transition S$_1$−S$_0$ takes place independently in the two halves, and thus the electronic mixing between the two chromophores in the S$_1$ states should be very small. This is supported by the fact that fluorescence from the S$_1$ state of the free base part exhibits the same spectral shape as that of the monomer. However, relaxation processes from the S$_1$ state are considerably affected by the

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(51) For the estimation of intramolecular energy transfer rates, the initial optical densities of T−T absorption at $t = 0$ were extrapolated from the time profile of the signals by using a least-squares method, assuming a first-order kinetics.

copper porphyrin counterpart. The lifetimes and quantum yields of the free base half are significantly reduced in the dimers. This can be mainly due to enhanced ISC in the dimers as being discussed in the following.

In general, fluorescence lifetime (τ_f) and yield (ϕ_f) are given by

$$1/\tau_f = k_r + k_{ic} + k_{isc} \qquad (1)$$

$$\phi_f = k_r/(k_r + k_{ic} + k_{isc}) \qquad (2)$$

where k_r, k_{ic}, and k_{isc} are radiative decay, internal conversion, and intersystem crossing rate constants, respectively. The radiative decay constants from the S_1 state should be the same between the monomer and the dimers since the absorption intensities of the S_1-S_0 transition of the free base part is considered to be the same among the three compounds. Thus, the decreases in lifetimes and quantum yields in the dimers are ascribed to an increase in k_{isc} and/or k_{ic}.

In some of gable-type porphyrins, fluorescence lifetimes of the free base homo-dimer are decreased compared to that of the corresponding monomer and exhibit a red shift of absorption Q-band spectra.[21,22] Therefore, an increase of k_{ic} is proposed in such dimers as a result of the formation of the dimer. However, in the present case, the free base homo-dimers do not show any change of the fluorescence lifetimes and any shift of absorption spectra in Q-band (<0.5 nm) compared to the monomer.[52] Thus, the observed decrease of the lifetimes in the hybrid dimers is indeed due to the presence of the copper(II) ion but not the formation of the dimer.

So far, numbers of zinc(II) porphyrin−free base porphyrin hybrid dimers with various spacers have been studied. In most of these dimers, singlet−singlet energy transfer from the zinc(II) porphyrin part to the free base is observed but lifetimes of the free base part are almost identical to those of corresponding free base homo-dimers. [7,9−10,21] This implies that neither k_{ic} nor k_{isc} in the free base part is affected by the zinc(II) porphyrin counterpart. In contrast to the zinc(II)−free base dimers, the present study shows that k_{ic} and/or k_{isc} is largely increased in the copper(II)−free base dimers depending upon the spacer molecule. Since the sizes and masses of zinc(II) and copper(II) ions are much the same, there could be only a slight difference in the vibrational structure of the two monomer metalloporphyrins. Indeed, resonance Raman spectra monitored at the S_1-S_0 transition are very similar to each other in terms of intensities and frequencies.[53] Since internal conversion is governed by the vibronic mixing between the S_0 and S_1 states, it is not probable that internal conversion of the free base part is significantly different between the two kinds of the dimers, namely, zinc(II)−free base and copper(II)−free base hybrid dimers. The main difference between zinc(II) and copper(II) ions is that only the copper(II) ion has an unpaired electron in the d_σ orbital. In fact, ISC of monomeric copper porphyrins occurs within a few picoseconds, while in zinc(II) monomers the ISC rate constant is approximately 2 ns. On this basis, we conclude that much faster radiationless decay in the copper−free base dimers is due to enhanced ISC but not to internal conversion.

Assuming that k_r and k_{ic} in the dimers are identical to those of the monomer, ISC rate of the dimer is described by using rate constants for the monomer,

$$\begin{aligned} k_{isc}{}^{D} &= \frac{1}{r}(k_r + k_{ic} + k_{isc}{}^{M}) - (k_r + k_{ic}) \\ &= \frac{1}{r}\frac{1}{\tau_f{}^{M}} - (k_r + k_{ic}) \end{aligned} \qquad (3)$$

where $k_{isc}{}^{M}$ and $k_{isc}{}^{D}$ are an ISC rate of the monomer and that of the dimer, respectively, $\tau_f{}^{M}$ is the fluorescence lifetime of the monomer, and r is a ratio of a fluorescence quantum yield of the dimer ($\phi_f{}^{D}$) vs that of the monomer ($\phi_f{}^{M}$),

$$r = \phi_f{}^{D}/\phi_f{}^{M} = \left(\frac{k_r}{k_r + k_{ic} + k_{isc}{}^{D}}\right)\Bigg/\left(\frac{k_r}{k_r + k_{ic} + k_{isc}{}^{M}}\right) \qquad (4)$$

Under the condition that $r \ll 1$, eq 3 can be rewritten as

$$k_{isc}{}^{D} \approx \frac{1}{r}\frac{1}{\tau_f{}^{M}} \qquad (5)$$

By using eq 5, the fluorescence lifetime of the monomer, $1/\tau_f{}^{M} = 8.0 \times 10^7\ s^{-1}$ and the observed values of r, 0.035 and 0.080, lead to $k_{isc}{}^{D}$ as $\sim 2.3 \times 10^9$ and $\sim 1.0 \times 10^9\ s^{-1}$ for Cu−Bz−H_2 and Cu−Np−H_2, respectively. Since $k_{isc}{}^{M}$ is estimated as $(6.5-7.0) \times 10^7\ s^{-1}$ from the monomer ISC yield $\phi_{isc}{}^{M} = 0.82-0.88$,[54,55] and $\tau_f{}^{M}$, it is found that ISC rates in the hybrid dimers are ca. 35 and 15 times of that of the monomer for Cu−Bz−H_2 and Cu−Np−H_2, respectively. The ISC yield of the dimer is described as

$$\phi_{isc}{}^{D}(H_2) = \frac{k_{isc}{}^{D}}{k_r + k_{ic} + k_{isc}{}^{D}} \qquad (6)$$

and thus, by using $k_r + k_{ic} = (1.0-1.5) \times 10^7\ s^{-1}$, the ISC yield of $\phi_{isc}{}^{D}(H_2) > 0.98$ is evaluated for both hybrid dimers.

Mechanism of Enhanced ISC. It is evident that enhanced ISC of the free base in the copper−free base dimers is not due to so-called “heavy atom effect” of the metal ion since copper is the nearest neighbor of zinc in the periodic table and ISC process in zinc(II)−free base dimers is not affected significantly. This argument is confirmed by our preliminary experiment in Pd(II)−Bz−H_2 dimer, which shows much the same lifetime of the free base, despite the larger atomic number of Pd. The mechanism that accounts for the enhanced ISC is discussed below.

In the case of the copper porphyrin monomer, exchange interaction between electrons in the half-filled copper d_σ orbital and porphyrin π orbitals makes porphyrin triplet states split into trip−doublet (^2T) and trip−quartet (^4T) states.[29−33,36] On the other hand, the singlet states in the porphyrin become sing−doublet (^2S) states as a whole of the system. Therefore, the ^2T states have configuration interaction with ^2S states via exchange interaction, and an electronic transition moment arises between the ^2S and ^2T states. This results in prompt ISC from $^2S_1$ to $^2T_1$ in copper porphyrin.[27,28] The ISC rate in a copper monomer is more than 3 magnitudes quicker than that of the free base porphyrins.

Compared with the copper monomer, enhancement of ISC rate of the free base in the hybrid dimers is much less, although

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it is not small at all. Similar to the case of the copper porphyrin monomer, exchange coupling between the triplet state of the free base and an unpaired electron in the copper(II) could play a role. However, in the case of the dimers, both exchange interaction (spacial interaction) and superexchange interaction (through bond interaction) will be possible.[52] As a result of such an interaction, the excited state of the dimer can be expressed by linear combination of doublet and quartet states as a whole, when the free base part is in the triplet and the copper(II) part is in the doublet ground state. The size of coupling in terms of the state's energy depends on the coupling term and the distance between the two chromophores and will give rise to splitting between the quartet and doublet states. Time-resolved EPR studies on the complexes, which consist of an excited triplet molecule and a doublet species, indicate the presence of the coupling,[16,56−58] although such coupling is considered to be too small to detect by optical measurements. Given this, the transition from S_1 to T_1 in the free base part slightly gains allowed character. Thus, the ISC process in the free base moiety is accelerated. Faster ISC in Cu−Bz−H_2 than that in Cu−Np−H_2 is reasonable since the smaller distance of the two halves should lead to a larger interaction.

Energy Transfer Yields from the Copper(II) Porphyrin to the Free Base Porphyrin. The T_1 state of the free base in the dimers is generated more than four times as large as that in the monomer, as can be seen in Figure 5. This is partially due to the enhanced ISC in the dimers as discussed above. In the monomer free base, ISC yield $\phi_{\mathrm{isc}}{}^{\mathrm{M}}(\mathrm{H_2})$, was reported as 0.82−0.88,[54,55] while $\phi_{\mathrm{isc}}{}^{\mathrm{D}}(\mathrm{H_2})$ is found to be almost unity in this work. Accordingly, in the dimer, the triplet formation yields cannot be expected more than 1.1−1.2 times greater than that of the monomer only by ISC process. Since the singlet−singlet energy transfer process is inconsistent with the fluorescence excitation spectra, triplet−triplet intramolecular energy transfer is very likely to cause larger T_1 yields in the hybrid dimers.

From the relative generated yields of the T_1 state, we estimate an efficiency of the triplet−triplet energy transfer. The ratio of the molecular extinction coefficients of TPPCu and TPPH_2 at 532 nm (18.8×10^3 cm^{-1}) is ca. 3:1 in the ground state. Photoexcitation at 532 nm produces the excited triplet manifolds of the copper moiety three times larger than that of the free base, since ISC yields are almost at unity in both halves. Taking account of difference of ISC yields between the monomer and dimers, the triplet yield is expected to be by 4.4−4.8 times larger than that of the monomer when energy transfer occurs with a 100% efficiency. These values agree with the observed value. Although the estimation may contain ~10% error from the uncertainty of the ISC yield of the monomer and the signal-to-noise ratios, it can be concluded the efficiency of intramolecular energy transfer is close to unity (> 0.9) in the two hybrid dimers.

Estimation of Energy Transfer Rates. As shown in Table 1, the relative initial optical density of T−T absorption of the hybrid dimers decreases as an increase of the pyridine concentration. A greater decrease is observed in Cu−Np−H_2 than in Cu−Bz−H_2. This implies that energy transfer is more retarded in Cu−Np−H_2 by the pyridine quenching process due to a slower energy transfer rate in this compound.

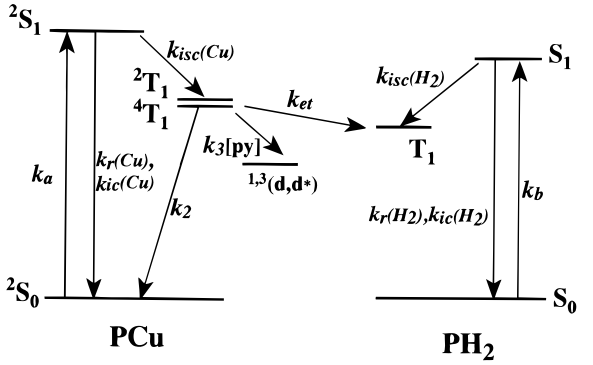

Figure 6. Scheme of relaxation and energy transfer processes in the copper−free base hybrid porphyrin dimers.

To estimate the energy transfer rate, k_{et}, we describe the relative triplet absorption intensity as a function of pyridine concentration, [py]. Herein, we define the relative triplet absorption intensity, I_{r}, as the absorption intensity per the unit concentration of the free base moiety. Figure 6 shows a schematic diagram of relaxation processes of the hybrid porphyrin dimers. The relative intensity of the T_1 free base consists of two contributions from ISC and from intramolecular energy transfer. Thus, the latter contribution is expressed by

$$\phi_{\mathrm{isc}}{}^{\mathrm{D}}(\mathrm{Cu})\,\frac{k_{\mathrm{a}}}{k_{\mathrm{b}}}\,\frac{k_{\mathrm{et}}}{k_{\mathrm{et}} + k_2 + k_3[\mathrm{py}]} \tag{7}$$

where k_{a} and k_{b} are the molar extinction coefficients to the S_1 states of the copper and free base halves, respectively, and k_2 and k_3 are the rate constants of the relaxation to the ground state and that of the quenching by pyridine in the copper part, respectively. $\phi_{\mathrm{isc}}{}^{\mathrm{D}}(\mathrm{Cu})$ is the ISC efficiency within the copper porphyrin, i.e., ISC from the excited sing−doublet state to the thermally populated trip−doublet and -quartet manifold. In eq 7, a difference of absorption coefficients between the free base and the copper moieties is taken into account. Since the relative intensity ascribed to the ISC within the free base half is given by $\phi_{\mathrm{isc}}{}^{\mathrm{D}}(\mathrm{H_2})k_{\mathrm{a}}/k_{\mathrm{b}}$, the total intensity of the triplet state $I_{\mathrm{r}}{}^{\mathrm{D}}([\mathrm{py}])$, is obtained as

$$I_{\mathrm{r}}{}^{\mathrm{D}}([\mathrm{py}]) = \phi_{\mathrm{isc}}{}^{\mathrm{D}}(\mathrm{H_2}) + \phi_{\mathrm{isc}}{}^{\mathrm{D}}(\mathrm{Cu})\,\frac{k_{\mathrm{a}}}{k_{\mathrm{b}}}\,\frac{k_{\mathrm{et}}}{k_{\mathrm{et}} + k_2 + k_3[\mathrm{py}]} \tag{8}$$

On the other hand, the relative triplet intensity in the monomer is simply written as

$$I_{\mathrm{r}}{}^{\mathrm{M}} = \phi_{\mathrm{isc}}{}^{\mathrm{M}}(\mathrm{H_2}) \tag{9}$$

From eqs 8 and 9, it follows that

$$\frac{I_{\mathrm{r}}{}^{\mathrm{D}}([\mathrm{py}])}{I_{\mathrm{r}}{}^{\mathrm{M}}} = A\,\frac{k_{\mathrm{et}}}{k_{\mathrm{et}} + k_2 + k_3[\mathrm{py}]} + B \tag{10}$$

where

$$A = \frac{k_{\mathrm{a}}\,\phi_{\mathrm{isc}}{}^{\mathrm{D}}(\mathrm{Cu})}{k_{\mathrm{b}}\,\phi_{\mathrm{isc}}{}^{\mathrm{M}}(\mathrm{H_2})} \tag{11}$$

and

$$B = \frac{\phi_{\mathrm{isc}}{}^{\mathrm{D}}(\mathrm{H_2})}{\phi_{\mathrm{isc}}{}^{\mathrm{M}}(\mathrm{H_2})} \tag{12}$$

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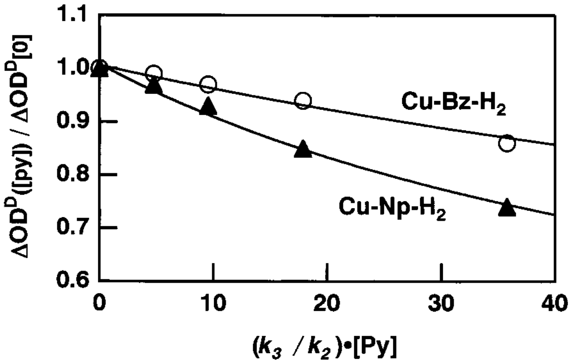

Figure 7. Plots showing the correlation of the initial transient optical densities with the pyridine concentration for Cu−Bz−H_2 (○) and Cu−Np−H_2 (▲). Solid lines show the best fitting curves for eq 13 by using parameters of $k_2 = 3.3 \times 10^{7}$ s^{-1}, $k_3 = 1.6 \times 10^9$ $(mol/L)^{-1}$ s^{-1}, $k_a/k_b = 3$, $A = 3.5$, and $B = 1.15$. Energy transfer rates, $(5.0 \pm 0.5) \times 10^9$ and $(1.9 \pm 0.4) \times 10^9$ s^{-1} were obtained for Cu−Bz−H_2 and Cu−Np−H_2, respectively.

Since I_r^M is constant, according to the definition above and I_r^D([py]) is proportional to the initial optical density of transient absorption of the dimer, ΔOD^D([py]), eq 10 is rewritten as follows.

$$\frac{\Delta OD^D([\mathrm{py}])}{\Delta OD^D(0)} = \alpha\left\{A\frac{k_{et}/k_2}{k_{et}/k_2 + 1 + k_3/k_2\,[\mathrm{py}]} + B\right\} \quad (13)$$

where $\Delta OD^D(0)$ is the initial optical density in 100% toluene solution. In eq 13, only two parameters, k_{et} and a, are unknown.[59] The relaxation rate constant of the copper porphyrin k_2 is the reciprocal of the lifetime. From the lifetime of 30 ns of the copper monomer at 300 K in toluene,[36−39] $k_2 = 3.3 \times 10^{7}$ s^{-1} is obtained. The quenching rate constant k_3 is determined by Stern−Volmer experiments for TPPCu and found to be 1.6×10^9 $(mol/L)^{-1}$ s^{-1}. This value is the same as the rate constant for the quenching by piperidine.[34] The value of k_a/k_b can be evaluated from the extinction coefficients of TPPCu and $TPPH_2$ at 532 nm and is to be ca. 3 as described in the previous subsection. ϕ_{isc}^D(Cu) and $\phi_{isc}^D(H_2)$ are equal to unity, while $\phi_{isc}^M(H_2)$ is 0.85 ± 0.03 as has been described. By using eqs 11 and 12, the values of 3.5 ± 0.2 and 1.15 ± 0.05 are obtained for A and B, respectively.

Figure 7 shows the plots of the relative initial intensity of T−T absorption, $[\Delta OD^D([py])/\Delta OD^D(0)]$ vs (k_3/k_2)[py]. By using a least-squares fitting, k_{et} was evaluated as $(5.0 \pm 0.5) \times 10^9$ and $(1.9 \pm 0.4) \times 10^9$ s^{-1} for Cu−Bz−H_2 and Cu−Np−H_2, respectively. Since the energy transfer efficiency ϕ_{ET} is given by $k_{et}/(k_{et} + k_2)$, the obtained values for k_{et} above led to $\phi_{et} \cong 0.99$ and $\cong 0.98$ for Cu−Bz−H_2 and Cu−Np−H_2, respectively. These agree with the result that $\phi_{et} \sim 1$ derived from the optical densities in the preceding subsection.

Comparison of Energy Transfer Rates between the Two Dimers. The larger energy transfer rate in Cu−Bz−H_2, derived above, is rationalized by a smaller distance of the two halves. In the case of through space energy transfer, both Förster and Dexter mechanisms predict a greater energy transfer rate with a smaller donor−acceptor distance.[60,61] In the Förster mechanism, energy transfer rate is proportional to R^{-6} (R is a distance between the donor and acceptor), while in the Dexter model, energy transfer rate decreases exponentially with an increase of R.

The Förster mechanism seems less feasible for our cases because of the negligibly small transition moment between the triplet and ground states in the energy acceptor, free base porphyrin. This is in line with the fact that the Förster mechanism mainly accounts for singlet−singlet energy transfer, which the dipole−dipole interaction governs. On the other hand, the exchange mechanism requires overlapping of the wave functions of the donor and acceptor and is considered to be inapplicable when the distance between the donor and acceptor is more than 5−10 Å. A molecular model calculation suggests that center-to-center distances are 10.8 and 13.4 Å, and edge-to-edge distances are 5.0 and 7.5 Å, for Cu−Bz−H_2 and Cu−Np−H_2, respectively.[62] With these donor−acceptor distances, it may be difficult to conclude that the Dexter mechanism operates by itself. Alternatively, a through-bond superexchange mechanism for long-range energy transfer can also open another channel.[63−65]

Since in both the Dexter and the superexchange mechanisms energy transfer rates are expressed by an exponential function of the distance, it seems impossible to draw a definite conclusion that only one of the two mechanisms is responsible. However, from a value of the prefactor of the distance dependence in the exponential function, we can discuss which of the mechanism is dominant for the observed energy transfer.

In the Dexter model, the prefactor of the distance between the donor and acceptor is described as $2/L$, where L is an effective Bohr radii.[61] Energy transfer rates, $k_{et}(1)$ for Cu−Bz−H_2 and $k_{et}(2)$ for Cu−Np−H_2, are given by

$$k_{et}(1) = A\exp(-2R_1/L)$$

$$k_{et}(2) = A\exp(-2R_2/L) \quad (14)$$

where A is a pre-exponential term and involves wave function overlap at $R = L/2$ and R_1 and R_2 are the distance between the donor and acceptor in Cu−Bz−H_2 and Cu−Np−H_2, respectively. A and L are identical between the two dimers since the constituents of the dimers and the dihedral angles between the two halves are the same. Therefore, the following relation is derived

$$k_{et}(1)/k_{et}(2) = \exp\{-2(R_1 - R_2)/L\} \quad (15)$$

From the calculated molecular conformation described above, a value of ∼2.5 Å is derived for $R_1 - R_2$ in terms of both edge-to-edge and center-to-center distances. By using this value and a value of 2.5 for $k_{et}(1)/k_{et}(2)$ estimated in the previous subsection, $L = 5.5$ Å is obtained from eq 15. For the Dexter systems studied to date, values of L have been reported as 0.9−1.8 Å.[14,66,67] It should be noted that even in the system consisting of coordination compounds that should have a rather large radii

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(59) a is given by a function of k_{et} and the other known parameters since the value of eq 13 should be 1 with [py] = 0. However, for our analysis shown in Figure 7, we assume that a is independent from k_{et} and we obtained the best fitting curves which pass through 1 at [py] = 0.

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due to a spatial distribution of electrons in question, L is reported at most as 1.8 Å.[67] The obtained value of 5 Å for L is apparently much larger than that observed for the systems where the Dexter mechanism dominates. This leads to the suggestion that a through bond (superexchange) mechanism is more likely to be dominant for the energy transfer rather than the Dexter (exchange) mechanism.

Recently, it is reported that π-conjugated spacer molecules mediate through bond electronic communication and excitation energy transfer.[8−11] Although the distance and orientation between the two halves are important factors in determining the coupling between the donor and acceptor, the bridging arene could also play key roles for the observed energy transfer.

5. Conclusion

In the present gable-type copper(II) porphyrin−free base porphyrin hybrid dimers, we have shown that intramolecular triplet−triplet energy transfer takes place with a very high efficiency (∼1). The energy transfer rate in the benzene-bridged dimer is estimated on the order of sub-nanoseconds and 2.5 times larger than that in the naphthalene-bridged dimer. From the distance dependence of the energy transfer rates, contribution of a through bond mechanism is suggested. On the other hand, ISC rates in the free base part are increased by 15−35 times compared with the monomer, depending upon the spacer. This enhancement of the ISC rates is induced by an unpaired electron in the copper ion of the counterpart. We propose that the unpaired electron increases a mixing between the S_1 and T_1 states of the free base half via a weak exchange coupling. It is shown that a copper ion plays a key role in the relaxation processes of the free base counterpart.

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